THE UNIVERSITY OF ALBERTA

KINETIC STUDIES ON THE HYDROLYSIS OF HALOPENTAMMINECHROMIUM (III) COMPLEXES

A THESIS

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T.P. JONES, B.Sc., A.R.I.C.

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ABSTRACT

The kinetics of the hydrolysis reactions of halopentamminechromium (III) complexes were investigated by both polarographic and spectrophotometric methods. The rate of hydrolysis is first order in chromium concentration and is independent of pH in the range 1 to 10. The rate constants for the aquation reaction are 5.6×10^{-4}, 6.3×10^{-3} and 6.0×10^{-2} min^{-1} for the chloro, bromo and iodo complexes at $25^{o}C$.

Above pH 11.5 the rate increased linearly with increasing hydroxide ion concentration. The second order rate constants for the chloro and iodo complexes are 0.11 and 220.1 $mole^{-1}$, min^{-1} resepectively.

From temperature studies, the activation energies, frequency factors and entropies of activation were eveluated for both the aquation and base hydrolysis reactions. The catalysing effects produced by both di and trivalent anions of various carboxylic acids resulted in a very rapid and linear rise in the reaction rate for salt concentrations of the same order as the reacting complex. This was interpreted in terms of the formation of ion pairs, which were able to facilitate the removal of the leaving group by charge transfer.

Independent proof of the existence of such ions pairs was obtained from the observed change in pH on addition of the chromium complex to a solution of the sodium salts of the various carboxylic acids.

It is believed that the mechanism of the aquation reaction involves participation of solvent water in the rate determining step, but not a direct bimolecular substitution by a water molecule. The name solvent assisted SN_1 best describes the mechanism of the aquation reaction.

The mechanism of the base hydrolysis reaction is believed to involve direct bimolecular substitution by hydroxide.

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I INTRODUCTION

General

In the last decade there has been increasing interest in the field of inorganic chemistry, especially in the study of the mechanism of substitution reactions in co-ordination complexes.

Two factors which have contributed towards the increased activity in this field are: a better understanding of the behavior of ions in solutions and better physical methods for following the reactions. Some of the new methods which have been used so successfully are: radiochemical methods, polarographic methods, nuclear and paramagnetic resonance and relaxation techniques. In addition, kinetic studies have been so extensive and fruitful in the field of organic chemistry, that it was a relatively easy problem to transfer at least a portion of the body of knowledge which has been developed by the organic chemist, to the field of inorganic chemistry. Kinetic studies are essential when studying the mechanism of chemical reactions. Thermodynamics, being interested only in the initial and final states of a system, gives little information about the mechanism of the process involved. An understanding of the mechanism of substitution reactions may enable one to predict the feasibility of searching for new compounds via a particular reaction route. This has been done by Basolo (1) in the

preparation of new complex compounds. Another factor which has contributed to the renaissance of this field, is the growth in our understanding of the factors which can affect chemical reactivity. In the field of inorganic chemistry much of this can be traced to the recent development of the Ligand Field Theory. (2) This is a combination of the old crystal field theory with molecular orbital theory. On the basis of Ligand Field Theory, it is possible to correlate many diverse properties of inorganic compounds with the electronic configuration of the metal atom. Among these are visible absorption spectra, magnetic behavior and stereochemistry. The contribution of this theory towards understanding the mechanism of substitution reactions will be discussed later.

Aquation Reactions

It is convenient to divide reactions of coordination compounds into the two main categories of substitution reactions and electron transfer reactions. Substitution reactions involve the replacement of one ligand by another or one metal by another. Using the terminology first put foward by Hughes and Ingold in describing organic reactions, these can be called SN and SE reactions respectively.

$$Y + M - X \rightarrow M - Y + X \qquad SN \qquad (I)$$

$$M' + M - X \rightarrow M' - X + M \qquad SE \qquad (II)$$

The terms SN and SE refer to nucleophilic substitution and electrophilic substitution respectively. A nucleophilic reagent donates electrons, while an electrophilic reagent acquires electrons.

The most common reactions of co-ordination complexes are nucleophilic substitution reactions, in which one ligand is replaced by another. The ligand is the nucleophilic reagent, as it donates a pair of electrons to the metal atom. Nucleophilic reactions can also be looked upon as acid-base reactions on the Lewis sense. The ligand is the base and the metal the acid.

Substitution reactions can be further subdivided according to the nature of the substituting reagent; solvolytic reactions, where the solvent is the substituting ligand and exchange reactions, where the substituting ligand is a ligand other than the solvent. In aqueous solution, solvolytic reactions are of the two kinds, aquation and base hydrolysis, shown in equations (III) and (IV).

$$M - X + H_2O \rightarrow MH_2O + X \quad \text{aquation} \qquad (III)$$

$$M - X + OH \rightarrow M - OH + X \quad \text{base hydrolysis} \qquad (IV)$$

Aquation involves replacement of a ligand by a water molecule, while the base hydrolysis reaction involves replacement by a hydroxide ion.

Most of the kinetic studies of substitution reactions have been directed towards obtaining an under-

standing of the mechanism of the aquation reaction, since it is believed that when one ligand is replaced by another, the reaction goes through the aquated complex. Thus it appears that this is the most common reaction of the co-ordination complexes in aqueous solution. For the reaction of chloropentamminecobalt (III) ion with sulphate, the reaction follows the path shown below.

$$Co(NH_3)_5Cl^{++} + H_2O \rightarrow Co(NH_3)_5H_2O^{+++} + Cl^- \qquad (V)$$

$$Co(NH_3)_5\ H_2O^{+++} + SO_4^{--} \rightarrow Co(NH_3)_5\ SO_4^{+} + H_2O \qquad (VI)$$

This is confirmed by the fact that the rate of such reactions is the same as the rate of aquation of the original complex (3).

In aqueous solution, the only possible exception to this observation occurs in the case of hydroxide ion as the attacking group. Even this is not fully agreed upon, as the kinetics also satisfy another mechanism which does require an aquo intermediate. The mechanism of the aquation reaction is therefore important in understanding the substitution reactions of co-ordination complexes.

From a knowledge of the mechanism of aquation reactions it is possible to predict the behavior of other reactions, as the kinetic behavior of the complexes is representative of the behavior of most inorganic compounds.

Aquation reactions are experimentally first order, with the rate depending only on the concentration of the complex. Such reactions are normally carried out

in water solution, and since the reactant, water, is in large excess, the reaction may in fact, be second or higher order, with the water playing a primary role in the transition state. The observed first order kinetics may, in fact, be only pseudo first order kinetics. Consequently, the kinetic studies will not yield any information about the overall molecularity, since the role of water in the rate determining step cannot be determined in any straight forward manner. One has therefore to resort to more indirect methods of approach to the problem, such as the effect of changing different variables on the rate of reaction. Some of the variables which have been investigated are, hydrogen ion, nature of the metal atom and ligand, stereochemistry, charge on the complex, π bonding, chelation, solvent, added electrolytes and isotopic studies.

Nucleophilic substitution reactions can proceed by at least two fundamentally different pathways, referred to by Hughes and Ingold as SN_1 and SN_2. SN_1 represents unimolecular dissociation mechanism, and SN_2 a bimolecular displacement mechanism. The first step in an SN_1 mechanism is a slow unimolecular dissociation, followed by a rapid reaction of M with Y, as shown in equations (VII) and (VIII)

$$M - X \xrightarrow{slow} M^+ + X^- \qquad \text{(VII)}$$

$$M^+ + Y^- \xrightarrow{fast} M - Y \qquad \text{(VIII)}$$

Since the intermediate in an SN_1 mechanism has a reduced co-ordination number, an original octahedral structure probably collapses to give some other configuration.

An SN_2 reaction, is one in which one group displaces another in a single step. This is shown in equation (IX)

$$M - X + :Y \longrightarrow Y:- - - -M- - -:X \longrightarrow M - Y + :X \qquad (IX)$$

In an SN_2 reaction the intermediate has an increase of one in its co-ordination number. For a bimolecular reaction, the incoming ligand participates in the rate determining step. Essentially, SN_1 mechanism involves bond rupture as the rate determining step, while for SN_2 mechanism, bond formation is the rate determining step. It should be possible to distinguish between these two mechanisms from the fact that in an SN_1 mechanism, the rate should be independent of the concentration and nature of the incoming ligand, while the opposite is true for an SN_2 mechanism.

In solvolytic reactions the displacing ligand is also the solvent, and consequently its role cannot directly be determined.

Conclusive proof of an SN_1 mechanism is the detection of an intermediate of reduced co-ordination number, but the converse to this is not true, since the

intermediate could be very reactive and perhaps survive only a few collisions, thus making it difficult to detect. Similarly, for an SN_2 displacement mechanism, an intermediate of increased co-ordination number could easily be the activated complex, and due to its reactivity, this could again avoid detection.

Even though, in the last decade, a considerable effort has been expended in trying to assign a mechanism to the aquation reaction, the exact path followed by this reaction is still open to question. This is probably due to the fact that the mechanism involves both SN_1 and SN_2 characteristics. It is then a matter of deciding which factor is the most important, bond breaking or bond making.

In an effort to understand the mechanism of aquation reactions, the effect of changing the variables mentioned earlier on the rate of aquation of some cobalt (III) ammine complexes has been studied.

On the basis of Ligand Field Theory, it has been possible to make semi-theoretical predictions about reaction rates, and reaction intermediates. (4) (5) The Ligand Field Theory is based on the fact that the d orbitals of a central metal atom which are degenerate in the gaseous state, are split, when in solution, as a result of the electrostatic field produced at the metal ion by the surrounding environment in the liquid. In a symmetrical octahedral environment, the d orbitals are split

into two groups. The orbitals lying in the direction of the ligand along the threefold axes, dz^2 and $dx^2 - y^2$, are raised in energy with respect to those lying away from the ligands, dxz, dyz and dxy. A diagramatic representation of this splitting is given in Fig. 1.

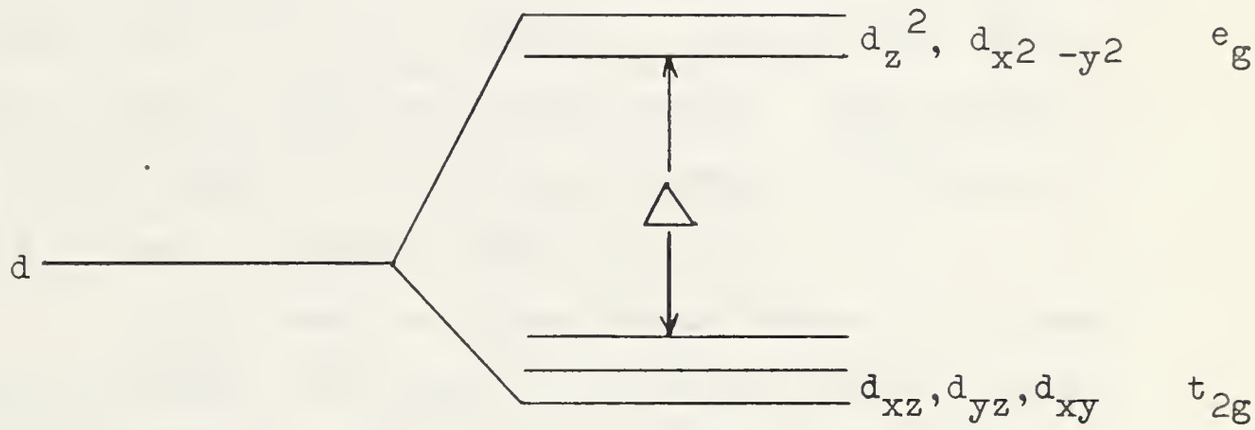


Figure 1. Energy level scheme for octahedral co-ordination

The total splitting between t_{2g} and e_g orbitals is called Δ. Electrons will tend to occupy the low energy orbitals and the gain in energy obtained by preferentially filling of these orbitals is called the Crystal Field Stabilization Energy (CFSE). This CFSE can be calculated from the position of the peaks obtained from the visible absorption spectra. (6)

The relative inertness of cobalt (III) and chromium (III) complexes, which have the configuration of $t_{2g}6$ and $t_{2g}3$ respectively, can be understood on the basis of an examination of the occupied orbitals. For the $t_{2g}6$ configuration, the d electron is maximal along

the threefold axis of the octahedron, and minimal along the bond directions. If the reaction involves an SN_2 path, the approaching reagent has to interact with the metal to give a 7 co-ordinate intermediate. For chromium and cobalt (III) complexes this can only be achieved by forcing electrons out of the t_{2g} into an e_g orbital, and this requires a fairly large activation energy. The approach of the seventh ligand to a bonding distance, is strongly resisted by the d electron along the axis.

On the basis of Ligand Field Theory it is possible to estimate the ligand field stabilization energy for the transition state, and thus measure the ligand field contribution to the activation energy. This has been done for the cobalt complex by Basolo and Pearson. (7). They have considered different possible configurations for the transition state by both SN_1 and SN_2 paths, and then calculated the gain in ligand field stabilization energy in forming these different transition states from an octahedral configuration. The difference in C.F.S.E. between the original octahedral complex and the transition state, was taken as the contribution ΔEa to the total activation energy of the reaction. From the potential energy function, Basolo and Pearson (8) have calculated the bond energies for the cobalt system, by using the Born approximation for the hydration energy of the complex ion. The

activation energies, including the contribution from C.F.S.E., are 121 k cal for SN_1 mechanism with trigonal bi-pyramid structure, 103 k cal for the SN_2 mechanism and 6-94 k cal for the SN_1 mechanism with square pyramid structure.

The activation energies for the aquation of cobalt (III) complexes are about 24 k cal. This rules out SN_2 mechanism and SN_1 via trigonal bi-pyramid. For an SN_1 mechanism, with the square pyramid structure, the activation energy 6-94 k cal represents the extreme limits, where the vacated position is occupied by water or left vacant. It appears that the most favourable path for the aquation reaction is through a square pyramid structure in which water is involved to some extent in the transition state. The above treatment is by no means rigorous, due to the fact that it is not possible to calculate the solvation energies of these complexes. On the other hand, if the solvent water does play an important role in the transition state by coming in to occupy the place of the leaving ligand, it is then a matter of choice whether the reaction be called SN_1 or SN_2. This would depend on whether a specific water molecule is involved or the solvation sheath in general.

It has been mentioned that in order to elucidate the mechanism of aquation reactions, the effect on the reaction rate of changing different variables has to be

examined. This has been lone for the cobalt (III) system.

The effect of increased chelation around the metal atom is to cause a small decrease in the rate of aquation. (9) If an SN_2 trans attack (trans position to the leaving group) mechanism was operative, then a decrease in the rate would be expected, as chelation would make it more difficult to attack the metal ion from the back side. The observed decrease in rate was much smaller than would have been expected on the basis of the steric influence of the chelating agents and was taken as an argument against SN_2 trans attack. Basolo and Pearson offer the argument that the transition state in an SN_1 mechanism is less stable for the chelated than for the non chelated complex, due to less efficient solvation. The larger the ion and the decrease in the number of N-H bonds then the less its solvation energy will be, and thus it will be less easily formed. The rate is therefore slowed down by chelation due to the reduced stability of the transition state. This shows the importance of ionic bond breaking in the transition state, but does not distinguish between SN_1 and SN_2 mechanisms.

The nature of the leaving group will affect the the rate of reaction, proceeding by both SN_1 and SN_2 mechanims, but not, perhaps, to the same extent. Lowering the charge and increasing the size of the leaving group, would

be expected to lead to a faster reaction by either mechanism. With very large groups it is possible that for steric reasons, an SN_2 mechanism may be hindered. For the halides, the rate order is iodide > bromide > chloride > fluoride as would be predicted by both mechanisms. This rate order correlates with the Ligand Field Strengh fluoride > chloride > bromide > iodide. This would indicate that the rate of reaction depends on the nature of the bond being ruptured. Basolo and Pearon (10) have investigated the aquation rate of a series of substituted pentammineacetato complexes of cobalt (III). The aquation rate parallels the acid ionization constants of the corresponding substituted acetic acids. Steric factors seem to play a very minor role in the reaction as trichloroacetato and trimethylacetato complexes, which are very bulky groups, seem to react at a rate expected on the basis of their K_a values. This normal rate, in the presence of bulky groups, argues against an SN_2 displacement mechanism by front side or cis attack, as it is sometimes called. The experimental observations do not exclude trans SN_2 attack or an SN_1 mechanism.

It has been observed that the monovalent dichloro complexes react about one hundred times faster than the divalent mono-chloro complexes (II). The aquation of the dichloro complexes takes place in two steps.

$$Co\ en_2\ Cl_2^{+} + H_2O \xrightarrow{k_1} Co\ en_2\ ClH_2O^{++} + Cl^{-} \quad (X)$$

$$Co\ en_2\ ClH_2O^{++} + H_2O \xrightarrow{k_2} Co\ en_2\ (H_2O)_2^{+++} + Cl^{-} \quad (XI)$$

$$k_1 \simeq 100\ k_2 \quad (XII)$$

The greater the charge on the complex, the more difficult it is to remove a negative group. From this observation it seems that bond breaking is more important than bond making.

Brown and Ingold (12) have investigated the kinetics of substitution of the dichloro bis-(ethylenediamine) cobalt (III) complex in the solvent methanol, using polarimetric, spectroscopic, chemical and radiochemical methods. It was found that in the presence of weakly nucleophilic anions, such as nitrate, chloride and bromide and thiocyanate, substitution took place at a rate independent of the nature and concentration of the added salts. For more strongly nucleophilic anions, such as nitrite, azide and methoxide, the rates were found to vary as a direct function of the nucleophilicity of the attacking groups. Ingold and Brown interpret the common rate observed with the weakly nucleophilic anions to indicate an SN_1 dissociation mechanism in the presence of these substituting anions whilst the faster rate with the more strongly nucleophilic anions is indicative of an SN_2 mechanism.

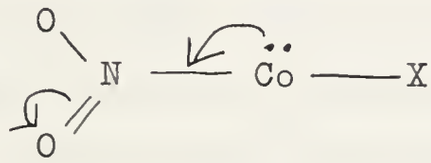
Basolo and Pearson (13) have shown that these data are also in agreement with an SN_2 mechanism involving the solvent methanol as the nucleophilic reagent. In methanol solution, the basic anions, such as azide and nitrite hydrolyse to give methoxide anions, thus the faster rate is due to direct substitution by the methoxide and not by the added anion. Basolo and Pearson working in buffered solutions of azide, nitrite and acetate, found that the reactions were very much slower than in unbuffered solutions. In the buffered solutions the concentration of methoxide ion was appreciably less than in the unbuffered solutions, thus accounting for the reduced rate.

Ingold (15) has followed a path which has been useful for studying organic reactions. Use is made of the different requirements of SN_1 and SN_2 processes in terms of electron displacement effects. In an SN_1 process the ligand leaves with its bonding electrons, so that any process which releases electrons towards the reaction centre, will assist the reaction. An SN_2 reaction requires electron withdrawal from the reaction centre to facilitate bond formation. Ingold has chosen the system Co·en AX where X is generally Cl, Br or NO_3, and studied the relation between the electron displacing properties of ligand A and the rates of hydrolysis. It has been observed that ligands which can release electrons

by a conjugative process to the reactive centre, give rise to an SN_1 mechanism.

i.e. 

Ligands which can withdraw electrons from the reaction centre favour the bi-molecular reaction



Therefore, by changing the nature of one of the non-labile ligands, it has been possible to change the mechanism of the reaction.

Ingold (16) has schematically illustrated the duality of mechanism in the variation of the rate of aquation, with polar effects of the orienting substituents in substituted halogeno-bis ethylendiammine-cobalt (III) salts. This is shown in fig. 2.

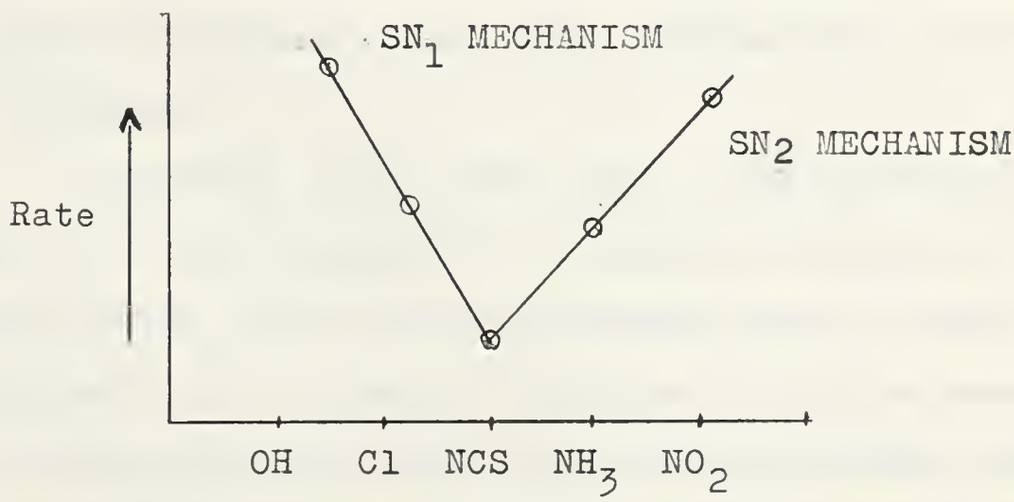


Figure 2. Rates of aquation of trans Co en_2 X Cl at 30°.

The decreasing rate along the SN_1 branch of the curve, can be understood in terms of the ability of the orienting substituent to supply electrons to the central metal atom. Hydroxide, which would be expected to produce the greatest polar effect in releasing electrons to the metal atom, thus produces the fastest rate, implying that the SN_1 mechanism seems to be important. At the other extreme, the nitro group would be expected to withdraw electrons from the metal atom. On the basis of an SN_1 mechanism, a decrease in the rate would be expected. This is contrary to what was observed. In order to explain the observed increase in rate with the nitro group, Ingold proposed that a bimolecular displacement takes place. The polar effect of the nitro group on the metal, would be expected to enhance attack by a nucleophilic ion. Ingold visualized this as bonding between the empty 4d orbitals of the metal ion and the incoming water molecule.

Recently, (17), (18), (19), (20) independent evidence has been presented for direct participation of solvent, water, in the rate determining step. Tobe (17) interpreted this as specific hydrogen bonding between the incoming water molecule, the departing ligand, and the amine group. This bonding is shown for Co en_2NH_3Cl in fig. 3.

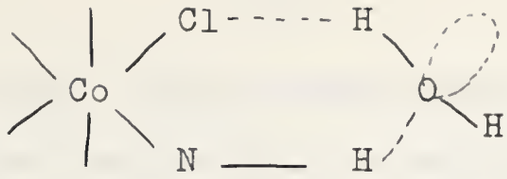


Figure 3. Hydrogen bonding for Co en_2NH_3Cl with a water molecule.

Less efficient hydrogen bonding for the Co $en_2NH_3NO_2$, is explained by suggesting that the terminal oxygen atoms of the nitrato group, have already taken advantage of their favourable position for hydrogen bonding with adjacent amino ligands, as shown in fig. 4.

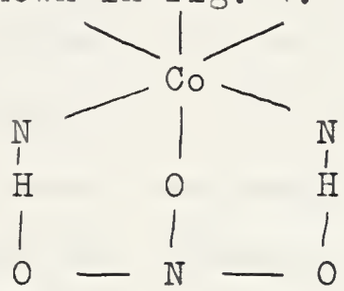


Figure 4. Hydrogen bonding between amino ligands and nitro group.

The evidence is supported by the fact that when the leaving group is varied from chloride to bromide to iodide, the activation energy increased, while the entropy of activation is markedly lowered.

Adamson and Basolo, (18), from both isotopic studies and solvent effects, have concluded that for the aquation of Co $(NH_3)_5$ Cl^{++} the results are consistent with a mechanism that involves solvent in the rate determining step.

Adamson (20) studied the substitution reactions of $Co(NH_3)_2(NCS)_4^-$ in different solvents and concluded that the reaction proceeds through a front

side bi-molecular displacement process, involving hydrogen bonding interaction between the anion and solvent. This mechanism which he designates as SN_2FS is identical with Tobe's (17) SN_2 mechanism.

Adamson's results (20) seem at variance with the data of Basolo and Pearson (10), on the acetate complexes, who observed that the rate of aquation was independent of the size of the leaving group, and concluded that the reaction probably did not involve front side attack by a water molecule. It is possible, however, that the water molecule enters the complex just after the bond which is being broken has stretched sufficiently. If this were so, then the size of the ligand would not be expected to affect the rate.

There doesn't seem to be a general rule that can be applied to cover the mechanism of all aquation reactions but it can be said that the mechanism involves participation of the solvent in the rate determining step. The extent of participation depends on the complex, especially the nature of the non-labile ligands. Whether the mechanism can be best described as SN_1 or SN_2 is a matter of choice.

Base Hydrolysis Reactions

The reaction of hydroxide ion with cobalt (III) ammines has received considerable attention in the last

decade (21). The reaction is commonly referred to as base hydrolysis. Even after a fairly thorough investigation, there still appears to be as much controversy as ever about the exact mechanism of this reaction.

One of the reactions most extensively studied has been that of the chloropentamminecobalt (III) complex with hydroxide ion. The rate of the base hydrolysis reaction is more than a million times faster than the aquation reaction. The simplest interpretation of the kinetics, is that the reaction involves a bi-molecular attack by hydroxide ion on the cobalt atom. However, the rate is dependent on the pH of the solution, even at pH values less than 3. If the mechanism involves a bi-molecular attack by hydroxide ion, it is surprising that at these low pH values the reaction takes place at all, since the concentration of the hydroxide ion is so small. F.J. Garrick (22), in 1937, observed a pH dependence for the hydrolysis of aquonitrotetramminecobalt (III) complex, even below a pH of 3. Garrick put forward a mechanism which involved a pre-acid equilibrium, followed by dissociation of the conjugate base. This has been designated as the SN_1 C B mechanism, where C B refers to the conjugate base.

The same mechanism is in keeping with the kinetics of the base hydrolysis of chlorpentamminecobalt (III)

complex, except that, in this case, the base removes a proton from one of the ammine nitrogens, forming an amido complex which rapidly dissociates.

$$Co(NH_3)_5Cl^{++} + OH^- \overset{fast}{\rightleftharpoons} Co(NH_3)_4NH_2Cl^+ + H_2O \qquad \text{(XIII)}$$

$$Co(NH_3)_4NH_2Cl^+ \xrightarrow[k_1]{slow} Co(NH_3)_4NH_2^{++} + Cl^- \qquad \text{(XIV)}$$

$$Co(NH_3)_4NH_2^{++} + H_2O \xrightarrow{fast} Co(NH_3)_5OH^{++} \qquad \text{(XV)}$$

For this mechanism Rate $= k_1 \left[Co(NH_3)_4NH_2Cl^+\right]$ (XVI)

$$= \frac{k_1 K_a}{K_w} \left[Co(NH_3)_5Cl^{++}\right]\left[OH^-\right] \qquad \text{(XVII)}$$

Where K_a is the acid dissociation constant of the ammine group and K_w is the ionic product of water.

For an SN_2 displacement mechanism:

$$\text{Rate} = k_2 \left[\text{complex}\right]\left[OH^-\right] \qquad \text{(XVIII)}$$

Thus, both SN_1 C B and SN_2 mechanism require the same kinetics with:

$$k_2 = \frac{k_1 K_a}{K_w} \qquad \text{(XIX)}$$

The SN_2 and SN_1 C B mechanisms are kinetically indistinquishable, and much of the available data on base hydrolysis can be explained by both mechanisms. For an SN_1 C B mechanism to operate, the complex must contain acidic protons. This has been proved by studying the hydrolysis of the bromopentacyano and bis (2, 2' bi-pyridine) dinitro

complexes of cobalt (III) at various pH. As expected, on the basis of an SN_1 CB mechanism, the rate was independent of the pH up to a pH of 10. Ingold (23), who strongly advocates an SN_2 mechanism for the base hydrolysis reaction, explains this by attributing the high rates for the hydrolysis of di pyridyl complex to promoted aquation, i.e. mechanism facilitated rather than one excluded. This, Ingold explains, is due to conjugation of the aromatic electrons with the bond which is being broken. Ingold indicated that the same pH independence is observed with trans chloronitro-bis-(ethylenediamine) cobalt (III) complex where nitrogen bound protons are available.

For the cobalt complexes there seems to be a difference of 10^7 or 10^8 between the rate of aquation and base hydrolysis.

$$\frac{k\ (\text{base hydrolysis})}{k\ (\text{aquation})} = 10^7 \text{ -- } 10^8$$

This large difference in rate is unexpected. It is possible to account for a factor of one hundred difference in the rate, from the fact that the conjugate base has a lower positive charge, which would facilitate release of a negative ion.

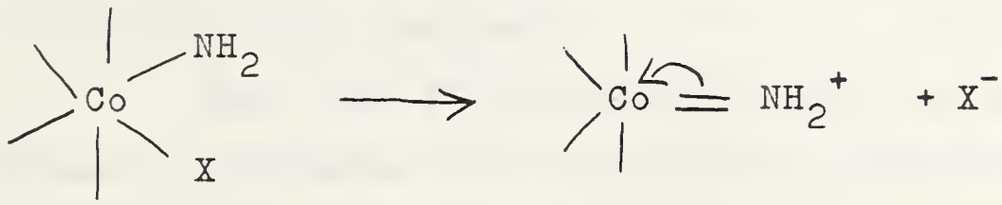
For both SN_1 aquation and base hydrolysis via SN_1 CB mechanism, the rate determining step in both cases is similar, i.e. dissociation of the cobalt to chlorine bond:

$$Co(NH_3)_5Cl^{++} \xrightarrow{k_1} Co(NH_3)_5^{+++} + Cl^- \quad \text{aquation (XX)}$$

$$Co(NH_3)_4NH_2Cl^{+} \xrightarrow{kcb} Co(NH_3)_4NH_2^{++} + Cl^- \quad \text{base hydrolysis (XXI)}$$

Another factor, which is believed to account for the unusual reactivity of the ammine complex, would be π bonding (24) in the reaction intermediate, or transition state.

This would facilitate the removal of halide, and stabilize the product as shown in equation (XXII).



(XXII)

π bonding involves partial transfer of p orbital electrons from ligand to the empty $d_{x^2-y^2}$ orbital of the metal atom. This would cause repulsion between the p_x orbital and the filled d_{xy} orbitals of the cobalt atom. This interaction would facilitate removal of the departing ligand to produce a five co-ordinate intermediate. The overlap between the metal $d_{x^2-y^2}$ and ligand p_x orbital, would tend to stabilize the intermediate. This effect is greater if the electron-donating ligand is cis (rather than trans) to the leaving group, since a trans ligand can only π bond to a p_y or p_z orbital and not to a p_x.

Attempts have been made to distinguish between SN_1 CB and SN_2 mechanism, from studies with deuterated complexes (25). The rate of reaction between $Co(NH_3)_5Cl^{++}$ and OD^- is about 60% slower than the reaction between $Co(NH_3)_5\ Cl^{++}$ and hydroxide ion. Unfortunately, so many

variables are changed, that the difference in rate can be accounted for by both SN_1 CB and SN_2 mechanism. It is not possible to examine the reaction between $Co(NH_3)_5Cl^{++}$ and OD^- since the rate of exchange of deuterium is faster than the rate of reaction.

Relatively few kinetic studies have been made on chromium (III) complexes.

Hamm (26), (27) has investigated the reaction between aquochromium (III) complex and a variety of anions such as citrate, oxalate and tartrate. He observed that the reaction was first order in chromium, and almost independent of the anion concentration.

Adamson and Wilkins (28) studied the rates of aquation and exchange of the thiocyanatopontammine complexes of both cobalt (III) and chromium (III). The aquation of the cobalt (III) thiocyanate complex was found to be catalysed by thiocyanate, while for the chromium complex, no such enhancement was observed. This was interpreted by proposing that the cobalt complexes undergo aquation by an SN_1 mechanism, whilst those of chromium aquate by an SN_2 mechanism.

Since there is a difference in electronic configuration between cobalt (III) and chromium (III), together with the fact that chromium complexes aquate faster than cobalt, it is conceivable that different mechanisms are involved in the aquation reactions.

Selbin and Bailar (29) have investigated the kinetics of aquation of cis cichloro-bis(ethylenediamine)-chromium (III) ion at a pH of 1.0. The aquation reaction proceeds in two steps, with the first step being ten times faster than the second. They were, therefore, able to follow aquation of the first chloride, without serious interference from aquation of the second. By analogy with the data for the corresponding cobalt complexes, they suggest that the complexes of the two metals follow similar mechanisms during aquation.

Macdonald and Garner (30) studied the kinetics of aquation of trans-dichloro bis(ethylenediamine) chromium (III) ion. On the basis that the rate is accelerated by ion-pairing and by light, they suggest that an SN_1 dissociation mechanism is involved in the aquation reaction, but that the possibility of an SN_2 mechanism is not ruled out.

Schlaeffer and King (31) have studied the kinetics of aquation of some chromium (ethylenediamine) complexes. The reaction takes place in two consecutive, first order steps. The first step involves breaking of one of the chromium to nitrogen bonds, to give the monoaquo species with one end of an ethylenediamine ligand free. The second step involves complete removal of the ethylenediamine ligand to give the di-aquo complex. The first step is approximately twenty five times faster than the second step.

The purpose of the work reported in this thesis was to further compare the chemistry of cobalt (III) and chromium (III) complexes so that a better insight could be obtained into the mechanism of the aquation reaction.

The compounds chosen for this study were the chloro, bromo and iodopentamminechromium (III) complexes for comparison with the corresponding cobalt (III) complexes. They were readily prepared and stable, provided they were stored in a dessicator in the dark. The chromium (III) complexes aquated at a sufficiently slow rate (32) that the reaction could be followed conveniently by conventional techniques.

Salt Effects

Salt effects have been widely used in elucidating the mechanism of reactions in solution (33).

The rate of reaction on the basis of the transition state theory, can be expressed by equation (XXIII).

$$k_s = \frac{RT}{Nh} \cdot K_s^{\ddagger} \frac{\gamma_A \gamma_B}{\gamma^{\ddagger}} \qquad \text{(XXIII)}$$

K_s is the thermodynamic equilibrium constant between the activated complex and the reactants A and B, γ_A, γ_B and $\gamma_{\ddagger}$ refer to the activity coefficients of reactants A and B and the activated complex respectively. Consequently, the rate of reaction is proportional to the concentration of the activated complex.

The rate expression can also be written according to equation (XXIV)

$$k_s = k_o \frac{\gamma_A \gamma_B}{\gamma^{\neq}} \qquad \text{(XXIV)}$$

where k_o is the rate constant at infinite dilution.

Since the activity coefficients are dependent on ionic strength, the rate of reaction will also depend on the ionic strength. For solutions of ionic strength less than .01 the Debye Huckel theory relates the activity coefficient of an ion to the total ionic strength of the solution by equation (XXV).

$$-\log \gamma = \frac{Z_i^2 \alpha \sqrt{\mu}}{1 + \beta a_i \sqrt{\mu}} \qquad \text{(XXV)}$$

μ is the ionic strength, a_i the distanceof closest approach of another ion to the ith ion, α and β are constants whose values depend on the solvent media. In water at 25° α is 0.509 x 2.303 and β is 0.329×10^8.

By substituting these values into equation (XXV) for the activity coefficient Bronsted (34) derived equation (XXVI) relating the rate of a reaction to the ionic strength.

$$\ln k = \ln k_o + 2 Z_A Z_B \alpha \sqrt{\mu} \qquad \text{(XXVI)}$$

k is the reaction rate constant of ions A with B at μ ionic strength. Z_A and Z_B are the charges of ions A and B respectively, k_o is the rate constant at infinite dilution.

Equation (XXVI) is only valid for dilute solutions, $\mu < .01$. This equation can also be derived on the basis of either collision or transition state theory. If log k is plotted against the square root of the ionic strength, the straight line observed should have a slope proportional to $Z_A Z_B$. The above relationship holds true for a number of reactions between ions (35).

According to their charge type, reactions should be accelerated (e.g. reactions between like ions) or retarded (e.g. reactions between unlike ions) or unaffected (e.g. when one of the reactants has no charge). These effects are called primary salt effects.

There are reported, in the literature, (36) many examples where the effect of ionic strength is not as predicted by the Bronsted equation. This is believed to be due to specific interaction, such as complex formation between ion reactant and added ions of the opposite sign. This destroys the agreement, and as such, has a considerable effect on the kinetics. Olson and Simonsen (36) have shown that, for the reactions between bromopentamminechromium (III) bromide with either mercurous or hydroxide ion (at ionic strength less than .01), the rate depends only on the concentration and nature of the added anions, and not on the total ionic strength of the solution. On this basis they suggest that the Debye Bronsted approach be abandoned, and that the rate be expressed by equation

(XXVII) which was first put forward by Acree (37).

$$k_{obs} = \alpha k_f + (1-\alpha) k_p \qquad \text{(XXVII)}$$

where k_f refers to the specific rate of the free ion and k_p the rate of the associated species; α is the degree of dissociation of the complex. Davies and Williams (38) have made a careful study of the reaction between bromo-pentamminecobalt (III) complex and hydroxide ion in the presence of sulphate. From solubility data, they were able to calculate the association constant between the bromo complex and sulphate ion. Thus, under particular conditions, it was known how much of the complex existed in the free ion, and how much as the associated species. Their results on salt effects are in agreement with Bronsted's theory, provided the associated species are treated as being kinetically distinct.

On the basis of the Debye-Bronsted equation, aquation reactions with the charge on the reacting water molecule being zero, would be expected to be insensitive to changes in ionic strength. This appears to be true when the added anions are perchlorate or other inorganic monovalent anions such as chloride and nitrate. Many investigators (39), (40), (41), have reported catalysing effects of different anions on the rate of hydrolysis of both cobalt (III) and chromium (III) complexes. Garrick (39) observed that sulphate had a marked accelerating effect on the rate of aquation of chloropentamminecobalt

(III) complex, whilst nitrate at an equivalent concentration had a very much smaller effect. Garrik attributed this to specific catalysis by sulphate ion, but he did not specify in what way the sulphate could catalyse the reaction.

Ikuta, McAdie and Smith (41) studied the effect of various electrolytes on the aquation of chloropentamminechromium (III) nitrate. Sulphate and iodate appreciably increased the rate of aquation whilst chloride and nitrate, had very little, if any effect on the rate. In the presence of perchlorate, a small decrease in the rate was observed. They were unable to explain these apparently specific salt effects.

Taube and Posey (40) studied the reaction between the aquopentamminechromium (III) complex and sulphate ion. The reaction was found to be independent of sulphate concentration above .01M. This was explained on the basis that the aquo complex formed an outer sphere complex or ion pair with the sulphate at low sulphate ion concentrations. This interpretation was confirmed by observations on the ultra violet absorption band of $Co(NH_3)_5H_2O^{+++}$ in the presence of varying amounts of sulphate ion. From Bjerrum's theory of ion association (42), it is possible to calculate, approximately, the extent of ion pair formation, if the charge and radius of both the complex and anion are known. From such calculation, trivalent complex cations are almost completely ion paired (with univalent anions) at a concentration of .01 M or higher, and even divalent cations

are significantly associated with divalent anions (e.g. $SO_4^{=}$) in this concentration range.

It therefore appears that association can take place between sulphate and divalent complexes of cobalt (III) and chromium (III), with the result that the ion pair seems to aquate at a faster rate than the free ion. With univalent anions, ion pairing does not take place to any great extent, thus explaining the insensitivity of the aquation reaction to added chloride, nitrate and perchlorate.

Basolo and Pearson (43) have studied the effect of added sodium azide on the rate of release of chloride from cis dichlorobis(ethylenediamine) cobalt (III) complex in methanol solution. At first, when concentration of azide is small, the rate increases markedly up to azide concentration of approximately 3×10^{-3} molar. Beyond this concentration, further addition has only a very small accelerating effect on the rate. This dependence of the rate on azide ion concentration can be explained on the basis of ion pair formation between the cobalt complex and azide ion. Up to a concentration of 3×10^{-3} M essentially two reactions are taking place. The hydrolysis of the free complex and the faster hydrolysis of the ion paired complex. Beyond .03 M, the complex is completely ion paired, and the rate is essentially independent of azide concentration above this concentration.

The purpose of studying salt effects on the aquation of $Cr(NH_3)_5Br^{++}$ was to further study the specificity that had been observed for the effect of anions on the rate of aquation. Before the present study was undertaken only the effects of a few anions on the rate had been investigated. The anions which had been employed were a number of inorganic monovalent anions which had little if any influence on the rate. Only two divalent anions had been investigated--sulphate and thiosulphate. These (41) showed a marked accelerating effect on the rate.

In this study the effect of a number of organic anions on the rate of aquation have been examined. This was made possible due to the fact that the aquation reaction is pH independent up to a pH of 10. By suitable choice of anions it was possible to vary a number of factors, such as the change, size and stereochemistry of the added anion. It was therefore, possible to gain an insight into the nature of the association between the complex and the anion.

II EXPERIMENTAL

Preparation of Compounds

$\left[Cr(NH_3)_5\ H_2O\right]\ (NO_3)_3 \cdot\ NH_4NO_3$.

Aquopentamminechromium (III) nitrate ammonium nitrate, was prepared (44) by reacting potassium chromium (III) sulphate twelve hydrate with a mixture of aqueous ammonia, and ammonium nitrate at 60° C. Air was passed through the resulting greyish-purple sludge to remove excess ammonia present. A measured excess of concentrated nitric acid was carefully added to the intense blue-violet solution with the temperature of the solution being maintained below 30° by cooling in an ice water mixture.

On cooling, orange crystals of aquopentamminechromium (III) nitrate ammonium nitrate separated out. These were filtered, washed with 95% ethanol, and air dried.

Analysis calculated for $\left[Cr(NH_3)_5\ H_2O\right](NO_3)_3 \cdot NH_4NO_3$ chromium 12.3%. Found for chromium-12.25%.

$\left[Cr(NH_3)_5Br\right]\ Br_2$.

Bromopentamminechromium (III) bromide was prepared according to the method described by M. Mori (44). A 1.0 M solution of aquopentamminechromium (III) ammonium nitrate in 4 M ammonia was allowed to react with 48% hydrobromic acid, and the reaction mixture allowed to digest on steam bath for 30 minutes. The pink crystals of bromopentamminechromium (III) bromide which separated out were

filtered off, washed with 95% ethanol, and air dried.

Analysis calculated for $\left[Cr(NH_3)_5\ Br\right]\ Br_2$. Chromium 13.8%. bromide 63.6%. Found for chromium 13.7%. bromide 63.7%.

$\left[Cr(NH_3)_5\ Cl\right]\ Cl_2$.

Chloropentamminechromium (III) chloride was prepared by a modification of the method described earlier for the bromopentamminechromium (III) bromide.

Aquopentamminechromium (III) ammonium nitrate (8.4 gm) was dissolved in a mixture of 10 ml water and 4 ml of 15M aqueous ammonia. To this mixture 25 ml of 37% hydrochloric acid and 20 ml of 95% ethanol were added.

On cooling, orange crystals of aquopentamminechromium (III) chloride precipitated out. The precipitate was filtered and washed with 95% ethanol. The dry aquochloride complex was then placed in a flask, and digested on a steam bath for 30 minutes, with a mixture of 30 ml water and 15 ml 37% hydrochloric acid. During digestion three 12 ml portions of concentrated hydrochloric acid were added at intervals of several minutes. After cooling to room temperature, the light pink crystals which had precipitated out were filtered off, washed with 95% ethanol and air dried.

Analysis calculated for $\left[Cr(NH_3)_5\ Cl\right]\ Cl_2$. Chromium 21.4 %. chloride 43.7%. Found for chromium 21.1% chloride 43.7%.

$\left[Cr(NH_3)_5\ Cl\right](CLO_4)_2$

Chlorpentamminechromium (III) perchlorate was prepared by rapidly dissolving 6 gm of the chlorochloride complex in 500 ml of water. The resulting solution was filtered and the filtrate treated with 100 ml of ice cold 70% perchloric acid. Upon cooling to 0^oC, chloropentamminechromium (III) perchlorate separated out. The pink crystals were filtered off, washed with 95% ethanol, and air dried. The perchlorate salt was found to be very unstable when exposed to direct light, and for this reason, it was always kept in a darkened dessicator.

Analysis calculated for $\left[Cr(NH_3)_5\ Cl\right](ClO_4)_2$. Chromium 14.0% chloride 9.60%. Found for chromium 14.1% chloride 9.50%.

$\left[Cr(NH_3)_5\ I\right]I_2$.

Iodopentamminechromium (III) iodide prepared in a manner similar to that described for the bromopentamminechromium (III) bromide, was kindly donated by Dr. W.J. Wallace.

Buffer Solutions.

Rate studies at low pH were made in perchloric acid and perchloric acid-sodium perchlorate mixture, and at pH 12 or higher in sodium hydroxide-sodium perchlorate mixtures. For the intermediate pH region, buffers were prepared by adding a sufficient amount of an appropriate amine

to 100 ml of 0.2 M perchloric acid solution to produce the desired pH. The pH values were determined by a Beckman model H2 pH meter. The resulting solution was diluted to 200 ml in a volumetric flask to give a final solution 0.1 M in perchlorate ion. With the exception of 2 aminopyridine, the amines were of spectral grade and were used without further purification.

Table I shows the amines used together with their buffer ranges.

TABLE I

USEFUL BUFFER RANGES OF THE VARIOUS AMINE-PERCHLORATE BUFFERS

Amine	Buffer-pH range	Kb
Pyridine	4 - 6	1×10^{-9}
2 aminopyridine	6 - 8	5×10^{-8}
ammonia	8 - 10	1.8×10^{-5}
diethylamine	10 - 12	1×10^{-3}

Analytical Methods

Chromium Analysis

Various methods for the determination of chromium in one of its complexes were tried. The most satisfactory results were obtained using the following prededure. About .3 gm of the complex salt was dissolved in 100 ml of 0.1M

sodium hydroxide, and boiled for ten minutes until precipitation of greenish-grey chromium hydroxides were complete. To the cooled solution 5 drops of 30% hydrogen peroxide were added and the solution was again boiled for ten minutes. During this time 2 drops of a 10% solution of nickel chloride were added as a catalyst to aid in the complete decomposition of any excess peroxide present. After cooling to room temperature, 25 ml of 0.5 M sulphuric acid, 10 ml phosphoric acid, and a measured excess of ferrous ammonium sulphate were added. The solution was then back titrated with standard potassium dichromate solution using sodium diphenylamine sulphonate as indicator.

Halogen Analysis

About 0.5 gm of the chromium complex salt was dissolved in water and diluted to 100 ml in a volumetric flask. Twenty-five ml aliquot of this solution were pipetted into 400 ml beakers, and approximately 25 ml of 0.2M perchloric acid added. The solution was then boiled for 10 minutes so as to release the bound halogen into solution.

After cooling to room temperature, the solution was diluted to approximately 300 ml and titrated conductimetrically with standard silver nitrate solution, using a conductimetric circuit described by Sand and Griffins (45).

Technique of Measurements

Spectrophotometric

Fig. 5 shows the absorption spectra of 10^{-2} molar

solutions of the iodo, bromo, chloro, aquo and hydroxy-pentamminechromium (III) complexes, obtained with a Cary model 14 recording spectrophotometer. It can be seen that in each case the halo complex absorbs at a longer wavelength than does the aquo complex and, as a consequence, the absorption maxima shift to shorter wavelength during the course of aquation. It should then be possible to follow the course of the reaction by observing the change in optical density at a particular, suitably chosen, wavelength. Consequently, in the preliminary work on aquation reactions the extent of the reaction was followed spectrophotometrically.

Solutions were prepared by mixing the required reagents in a 50 ml volumetric flask, with sufficient halopentamminechromium (III) salt to give a final solution 2×10^{-2} molar in chromium. The flask, which was darkened to eliminate any photochemical reaction (46), was transferred to a constant temperature bath, maintained to within $\pm .05^{\circ}$ of the desired temperature with a Sargent thermonitor temperature control.

When the solution had attained bath temperature, a 5 ml aliquot was withdrawn, transferred to a 1 cm quartz cell, and its spectrum recorded against distilled water in the reference beam. Subsequently, further samples were withdrawn at known times, and their spectra determined. The reaction was proceeding slowly enough that no significant reaction occurred in the time required to obtain the spectra.

Figure 5.

Absorption spectra of aquo, hydroxy and halopentammine-chromium (III) complexes.

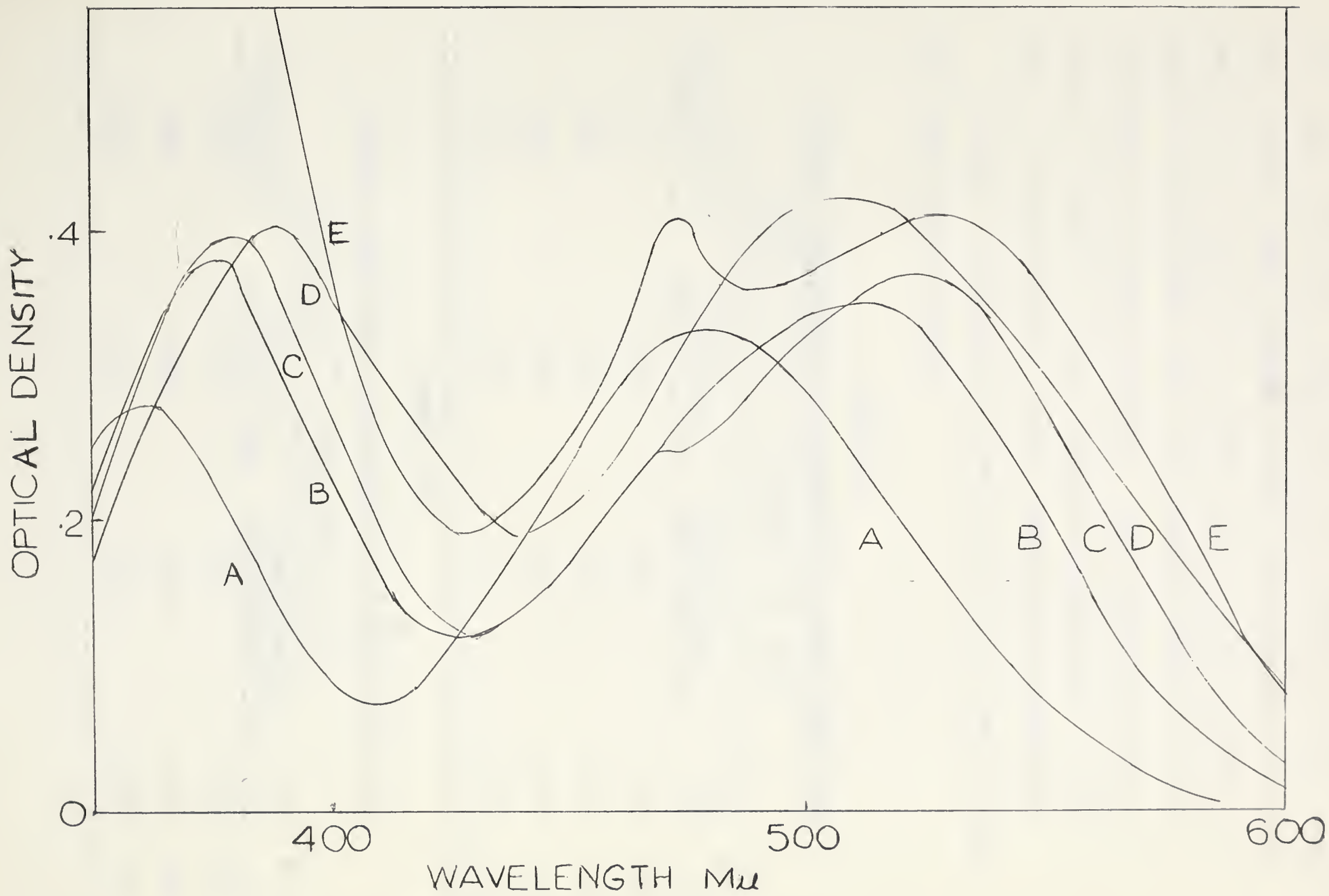
A. 10^{-2} M $Cr(NH_3)_5 H_2O^{+++}$ in a 1 cm. cell. Absorption maxima at 360 and 479 m

B. 10^{-2} M $Cr(NH_3)_5 Cl^{++}$ in a 1 cm. cell. Absorption maxima at 375 and 512 m

C. 10^{-2} M $Cr(NH_3)_5 Br^{++}$ in a 1 cm. cell. Absorption maxima at 378, 468 and 523 m

D. 10^{-2} M $Cr(NH_3)_5 OH^{++}$ in a 1 cm. cell. Absorption maxima at 399 and 507 m

E. 10^{-3} M $Cr(NH_3)_5 I^{++}$ in a 10 cm. cell. Absorption maxima at 471 and 528 m


OPTICAL DENSITY
·4
·2
0
400
500
600
WAVELENGTH Mμ
A
B
C
D
E
A
B
C
D
E

Solutions of known but different concentrations of both aquo and chloro complexes were prepared. Their absorption spectra were recorded at 25°C in 1.00 cm corex cells. The optical densities read from the recorded spectra at specific wavelengths were then plotted against the concentration of complex present. These data are given in tables II and III and are displayed graphically in fig. 6 and 7, for the aquo and chloro complexes respectively.

A linear relation was observed in both cases showing that Beer's Law was valid.

TABLE II

OPTICAL DENSITIES AND EXTINCTION COEFFICIENTS FOR $Cr(NH_3)_5 H_2O^{+++}$ SOLUTIONS AT 25°C.

Concentration (molar)	Optical Density D_{520}	Extinction coefficient ϵ_{520}	D_{480}	ϵ_{480}
.0113	.252	22.4	.418	37.1
.0200	.430	21.5	.690	34.5
.0230	.491	21.4	.803	35.0
.0373	.821	22.0	1.389	34.6

TABLE III

OPTICAL DENSITIES AND EXTINCTION COEFFICINTS FOR $Cr(NH_3)_5 Cl^{++}$ SOLUTIONS AT 25°C.

Concentration (molar)	Optical Density D_{510}	Extinction coefficient ϵ_{510}	D_{550}	ϵ_{550}
.0165	.390	23.3	.592	35.8
.0200	.360	23.0	.720	36.0
.0333	.771	23.1	1.199	36.3

Figure 6.

Plot of optical density against concentration for $Cr(NH_3)_5 Cl^{++}$

A. Optical density measured at 510 mμ

B. Optical density measured at 550 mμ

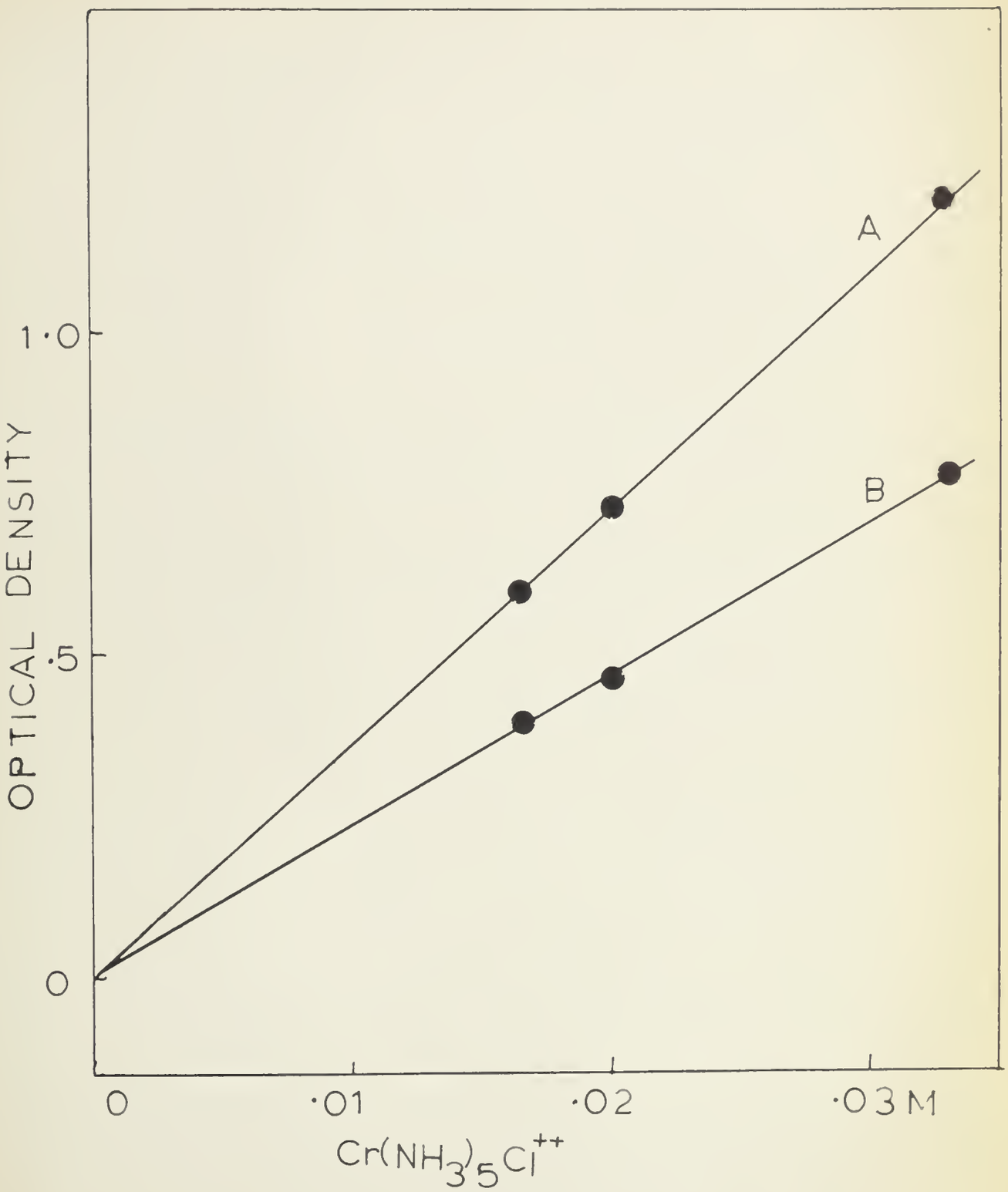
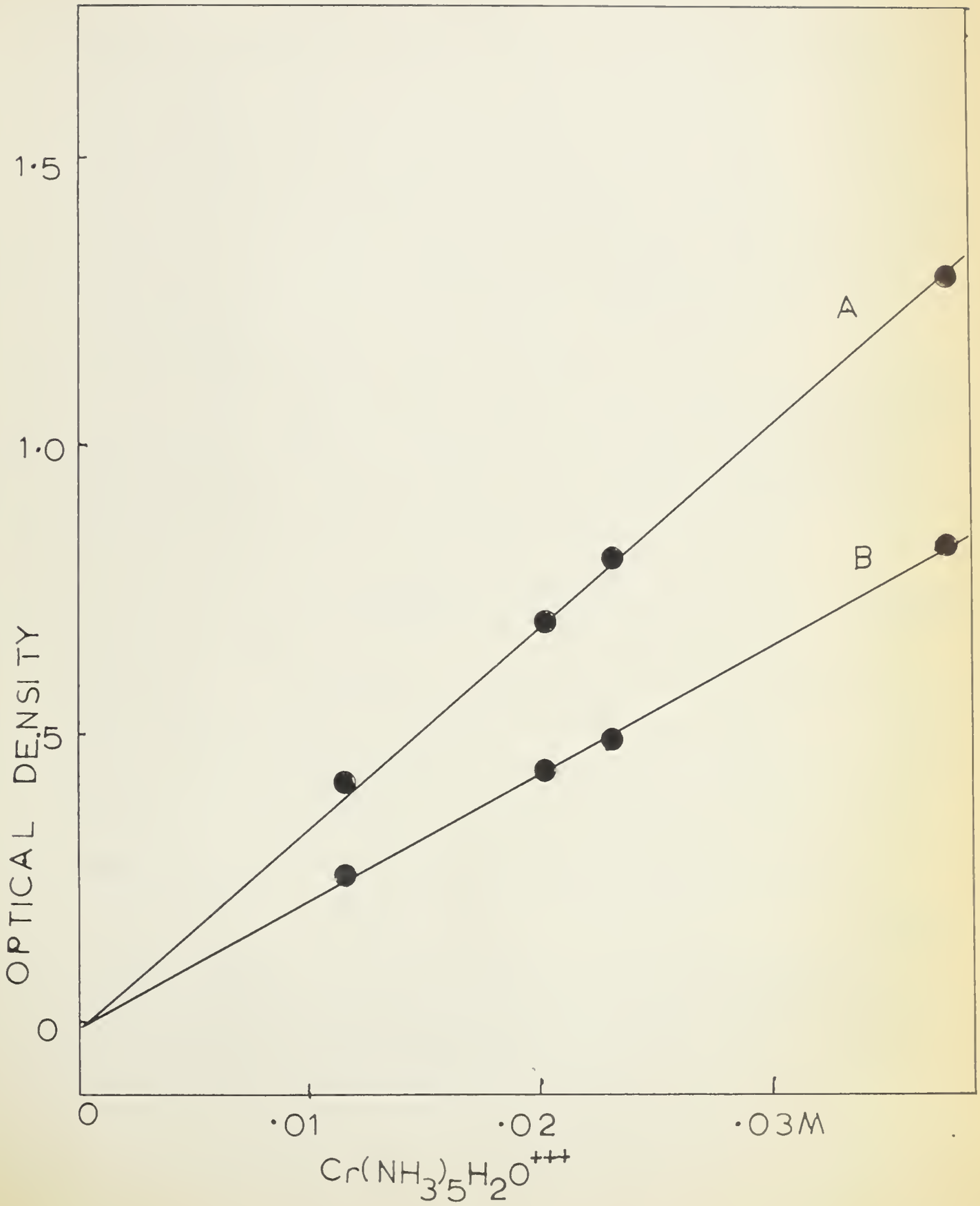

A
B
1·0
·5
0
OPTICAL DENSITY
0
·01
·02
·03 M
$Cr(NH_3)_5Cl^{++}$

Figure 7.

Plot of Optical density against concentration for $Cr(NH_3)_5 H_2O^{+++}$

A. Optical density measured at 480 mμ

B. Optical density measured at 520 mμ


1·5
1·0
·5
0
OPTICAL DENSITY
A
B
0
·01
·02
·03M
$Cr(NH_3)_5H_2O^{+++}$

Determination of Rate Constant

Once the spectra had been obtained, several wavelengths were selected at which the optical density was to be measured. These were chosen so that an appreciable difference in optical density between the reactant and product was obtained. It was at the same time desir[illegible] to select wavelengths around the peak maxima of the curves to eliminate errors that would be introduced by reading the optical density on the steep portion of the curve. The wavelengths which were used for following the aquation of the chloro complex were 550 mμ and 390 mμ .

The specific rate constant was then calculated from the measured optical densities as follows. For a first order reaction, the specific rate constant k can be expressed in the form of equation (XXVIII).

$$k = \frac{2.303}{t} \log \frac{c_o}{c} \qquad \text{(XXVIII)}$$

Where c_o is the original concentration of the reactant, c the concentration of reactant at any time t and k the specific rate constant. It has been shown above that the concentration of the reacting species is linearly related to the measured optical density as given by equation (XXIX).

$$D = \epsilon\, lc \qquad \text{(XXIX)}$$

In this equation ϵ is the molar extinction coefficient, l the thickness of the absorbing medium and c is the molar concentration of the absorbing species.

At the instant of initiation of the reaction, all of the reactive species is present in the original form. Thus, original concentration of the reactant (c_o) is equal to the total concentration of chromium added, and the original concentration of the product (c_2^o) is zero.

Hence, the optical absorption characteristics of the solution are accurately represented by equation (XXX).

$$D_1^o = \epsilon_1 \, l c_1^o \qquad \text{(XXX)}$$

At infinite time, only the product was present, and the optical absorption characteristics may be accurately represented by equation (XXXI).

$$D_\infty = \epsilon_2 \, l c_1^o \qquad \text{(XXXL)}$$

Where ϵ_2 is the molar extinction coefficient of the product.

In the reactions studied $c_1^o = c_2$ since one molecule of reactant gives one molecule of product and, as a consequence, equation (XXXI) transforms to equation (XXXII).

$$D_\infty = \epsilon_2 \, l c_1^o \qquad \text{(XXXII)}$$

At any intermediate time t, both reactant and product will be present in the solution and each will absorb incident radiation of a particular wavelength, in a characteristic way dependent upon its concentration. The total optical density of the solution is then equal to the sum of the optical densities of both reactant and product present as indicated in equation (XXXIII).

$$D = D_1 + D_2 \qquad \text{(XXXIII)}$$

From equation (XXIX)

$$D_1 = \epsilon_1 \, lc_1 \qquad \text{(XXXIV)}$$

and

$$D_2 = \epsilon_2 \, lc_2 \qquad \text{(XXXV)}$$

But $c_2 = (c_1{}^o - c_1) = (c_o - c)$ (XXXVI)

where c is the concentration of reactant present at time t.

When D_1 and D_2, from equation (XXXIV) and (XXXV) are substituted in equation (XXXIII) the result is whown in equation (XXXVII).

$$D = \epsilon_1 \, lc + \epsilon_2 \, l(c_o - c) \qquad \text{(XXXVII)}$$

Substitution for ϵ_1 and ϵ_2 from equation (XXX) and (XXXII) yields equation (XXVII).

$$D = l \left[\frac{D_o c}{lc_o} + \frac{D_\infty (c - c_o)}{lc_o} \right] \qquad \text{(XXVIII)}$$

Which on simplifying gives equation (XXXIX).

$$\frac{c_o}{c} = \frac{D_\infty - D_o}{D_\infty - D} \qquad \text{(XXXIX)}$$

Equation (XXXIX) is then substituted into the rate equation for a first order reaction to yield equation (XL).

$$k = \frac{2.303}{t} \log \frac{D_\infty - D_o}{D_\infty - D} \qquad \text{(XL)}$$

Plot of $-\log (D_\infty - D)$ against time gives a straight line provided the reaction is first order. The above procedure was then repeated at other wavelengths and the mean value of the rate constant determined from the slopes.

$$\text{Slope} = \frac{k}{2.303} \qquad \text{(XLI)}$$

D_∞ was measured by preparing a solution of the pure product i.e. aquopentamminechromium (III) salt of the same concentration as the reactant, and measuring its absorption spectrum under the same conditions. It was not possible to use the D_∞ value obtained by carrying the reaction to completion, because of slow subsequent decompostion of the aquopentamminechromium (III) complex. During a kinetic run it was not necessary to correct for the decomposition of the aquo complex, as the reaction was only followed for about one half life. During this time, little or no decomposition of the aquo complex was observed.

There is considerable overlapping of the absorption curves for the halo and aquo complexes, and the observed change in optical density is small. This is especially true for the aquation of chloropentamminechromium (III) complex. Another factor which could affect the precision of the measurements is the conversion of the product aquopentamminechromium (III) complex to other products, whose optical absorption characteristics are not known sufficiently well to be amenable to easy correction of the total optical density. Thus, hydrolytic removal of ammonia is known to occur (47). This latter reaction is sufficiently slow, that in acid solution, no significant error is introduced but in near neutral or alkaline solutions (48) insoluble hydroxo species are formed from

these hydrolysis products, and the solution becomes optically opaque.

Other disadvantages of the spectrophotometric method include experimental difficulty in maintaining the the cell compartment of the spectrophotometer at a constant temperature, which is low enough to quench the reaction. This is very important in studying the hydrolysis of the iodo and bromo complexes since the reaction, even at room temperature is fast enough for significant reaction to have occurred during the time required for recording the spectrum. It is apparent, that the spectrophotometric method for following the hydrolysis of halopentamminechromium (III) complexes has very limited applications, and thus recourse was had to a polarographic technique.

Polarographic Measurements

Although it is well known that many complex compounds (48) are polarographically reduced at the dropping mercury electrode, relatively few applications of polarography for following kinetics of reactions are reported (49), (50), (51). One of the probable reasons for this has been that, with the conventional H polarographic cell which is commonly used for polarographic measurements, it is almost impossible to make a repeated series of measurements quickly. The difficulty lies in the fact that the reference electrode is a part of the H cell, thus, after each measurement, the cell has to be rinsed out and dried before further measurements can be made.

Harris (52) has overcome these difficulties by constructing a polarographic cell in which the reference electrode is connected to the solution container by means of a flexible salt bridge(54).

Fig. 8 shows a sketch of the simple polarographic cell used.

The polarographic cell is made up of three distinct components; the saturated calomel reference half cell A, the electrolysis cell E, and a rubber stopper H, which served as a lid for the electrolysis cell.

The saturated calomel half cell A was prepared in the conventional way, but using a 15 ml distillation flask with a shortened side arm (15 mm) as a container.

The electrolysis cell E (25 x 80 mm) was made from a (25 x 150 mm) test tube. The rubber stopper lid H was provided with three holes, one of which was fitted with a 100 mm glass delivery tube F to which a few millimetres of thermometer capillary were sealed as shown in fig. 8. The thermometer capillary provided a more efficient deaeration. It has been observed (53) that a fast stream of very small bubbles is most effective in removing dissolved air. In this way, it was possible to deaerate the solution in less than two minutes, thus making it possible to do polarographic measurements rapidly.

One of the two remaining holes in the rubber stopper was fitted with a (100 x 10 mm) fine sintered glass tube D, which served to provide electrical contact between the salt

Figure 8.

The Polarographic Cell

A. Saturated calomel half cell.

B. Flexible salt bridge.

C. Porous glass plug.

D. 1 cm sintered glass tube.

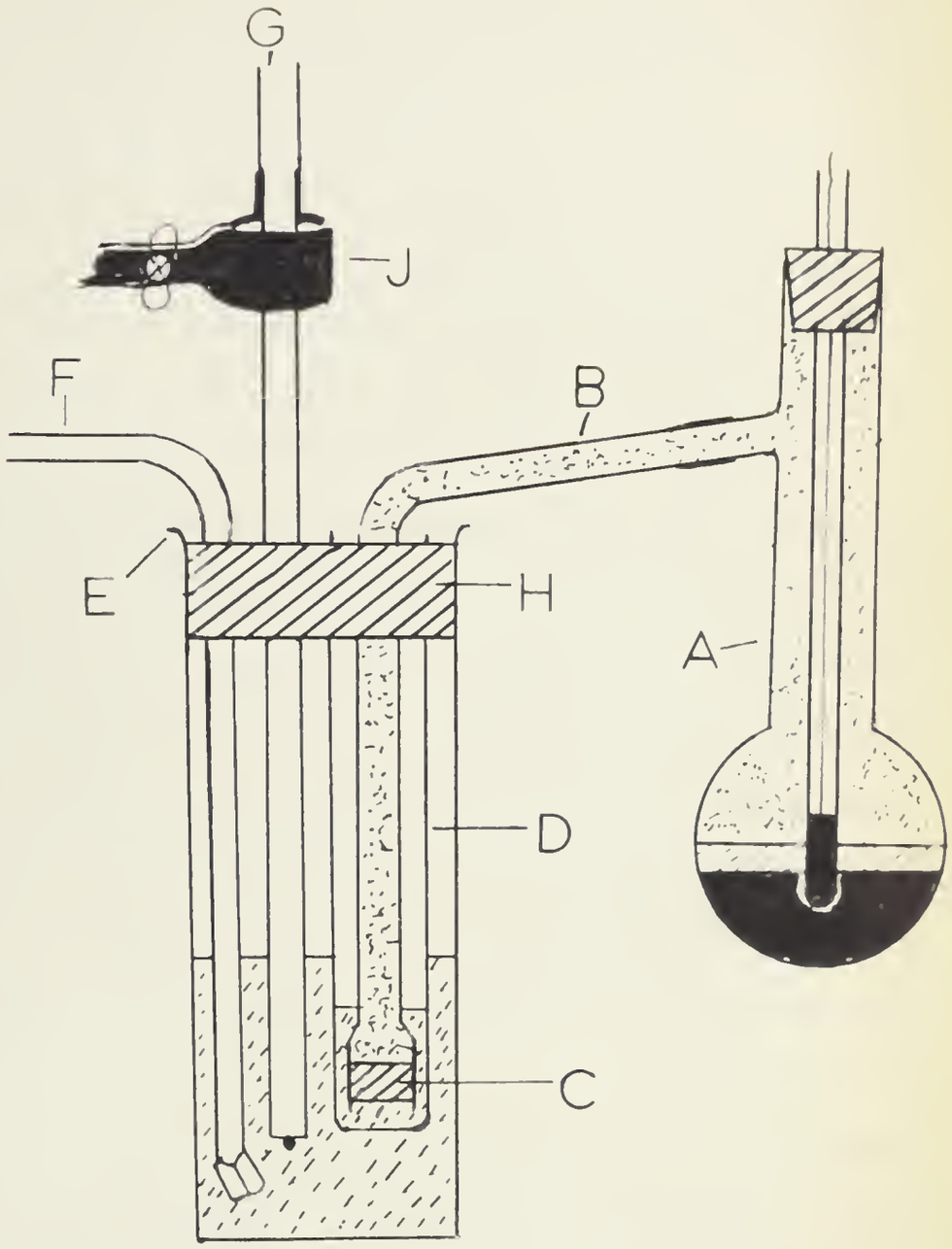
E. Electrolysis cell. (25 x 80 mm)

F. Bubbling Tube.

G. Dropping mercury electrode.

H. 3 hole rubber stopper

J. Clamp.


G
J
F
B
E
H
A
D
C

bridge B, and the electrolysis cell E. Both the bubbling and the sintered glass tubes were permanently attached to the rubber stopper H.

The clamp J, situated above the electrolysis cell, as shown in fig. 8, held in position a one hole rubber stopper, through which the dropping mercury electrode was passed. This was provided to keep theelectrode vertical and also so that the electrode could be lowered to the same height each time. It is important in polarographic measurements to keep the height of the mercury column constant, and the electrode vertical , as both these factors can affect the drop time which directly affects the diffusion current.

Electrical contact between the saturated calomel half cell A, and the electrolysis cell was provided by means of a flexible salt bridge B (54) made from 17 cm of 3 mm gum tubing terminated with a porous glass plug. All the polarograms were recorded at $0^{o}C$, with the electrolysis cell contained in a $0^{o}C$ temperature bath, made with ice - ice water mixture in a 5 litre dewar flask. The dewar flask was fitted with a perspex disc which carried nine holes in which the electrolysis cells fitted.

Recording of the polarograms at $0^{o}C$ instead of at $25^{o}C$, as is more common, offered three important advantages.

(a) the hydrolysis reaction was effectively quenched even in the case of the iodo complex.

(b) less maximum surpressor was required, and this was very desirable since maximum surpressors have a tendency to distort the polarographic wave.

Since the chromium reduction waves are irreversible (55) the half wave potential is slightly more positive at low temperatures due to the reduction process becoming more reversible. The wave is thus sharper and facilitates measurement of the diffusion current.

(c) at $0^{o}C$ at constant temperature bath can be made simply and effectively with ice-ice water mixture in a dewar flask.

The cell described above has the advantage over the familiar but cumbersome H cell in that a series of measurements could be made quickly by simply replacing the electrlysis cell each time.

Kinetic Measurements

The technique for preparing the solutions to be studied was essentially that described for the spectrophotometric measurements. The required reagents and sufficient halopentamminechromium (III) salt were mixed in a 50 ml volumetric flask and diluted to volume so that the final concentration of complex was 10^{-3} molar.

The flask was then wrapped in aluminum foil to eliminate any photochemical reactions, and then transferred to a water bath which was thermostated to within $\pm$ $.05^{o}$ of the desired temperature, by means of a Sargent thermonitor temperature controller. After the solution had reached bath temperature 5 ml aliquots were pipetted out and transferred to a polarographic electrolysis cell maintained at $0^{o}C$ in an ice-ice water mixture, temperature bath. One drop of $\frac{1}{2}$% gelatin solution was added as maximum surpressor and sufficient

concentrated sulphuric or perchloric acid to completely neutralize any base present and leave the final solution 0.1M in hydrogen ion. The amount of acid to be added was calculated from the amount of base present.

While investigating the effect of sulphate on the hydrolysis of bromopentamminechromium (III) complex, it was observed that the difference in half wave potentials of the bromo and aquo complex was greater in a sulphate medium than in perchloric acid. This facilitated measurement of the diffusion current of the bromo complex. The reason for this shift in half wave potential is believed to be as a result of ion pair formation between the complex salt and sulphate. This will be discussed more fully when considering the effect of anions on the half wave potential of $Cr(NH_3)_5 Br^{++}$. As a result of this observation, sulphuric acid was added as inert electrolyte in all subsequent determinations.

The rubber stopper with the attached bubbling and sintered glass tube was then introduced into the electrolysis cell. By applying suction at the mouth of the sintered glass tube, some of the solution from the electrolysis cell was sucked up into the sintered tube so that when the flexible salt bridge was inserted, the electrical circuit was completed as shown in fig. 8.

Purified nitrogen, previously cooled to 0° by passing through six feet of copper coil immersed in ice ice water mixture, was passed through the solution for three minutes by means of bubbling tube F. After deaeration with

nitrogen, the dropping mercury electrode was introduced into the solution and the polarogram recorded on a Leeds and Northrup type E Electrochemograph.

By having available a few dozen electrolysis cells and two rubber stoppers with the required attachments, it was possible to make a polarographic measurement every 5 minutes. This was achieved in the following way: Whilst one sample was being polarographed, a second sample was deaerated in another electrolysis cell. The dropping mercury electrode and the flexible salt bridge were withdrawn from the first cell, rinsed with water, and wiped dry with tissue paper before inserting into the second electrolysis cell. The second sample was then polarographed.

The rubber stopper, from the first cell, was then rinsed with water, wiped dry, and introduced into the next sample to be polarographed.

Since the time that it takes for the polarogram to be recorded is about 4 minutes, it was possible to obtain a polarogram every 5 minutes.

Most of the kinetic studies were made on the aquation of the bromo complex at 25°C, which had a half life of about 1½ hours. The reaction was usually followed for two half lives with aliquots being withdrawn for analysis every half hour.

Since a polarographic analysis can be made in 5 minutes, it was then possible to follow six separate kinetic runs simultaneously. The six reaction mixtures were prepared

at five minute intervals, and aliquots were withdrawn for analysis from them in order, at consecutive five minute intervals. In this way each of the solutions was analysed every half hour.

The number of runs that could be made simultaneously was dependent on how fast the reaction was, and how often readings were taken.

The above technique was slightly modified when following rather fast reactions, such as the base hydrolysis of the iodo complex.

Fifty ml. of solution containing the necessary reagents was brought to bath temperature in a (250 x 25 mm) pyrex test tube.

After the solution had attained bath temperature, a weighed sample of the iodo complex was added and, quickly dissolved. Aliquots were then quickly withdrawn with a 5 ml pipette whose end had been cut off in order to make a fast transfer of the solution to the electrolysis cell. So as to effectively quench the reaction, the electrolysis cell, which was immersed in the $0^{o}C$ water bath, contained the necessary amount of acid to give a final solution approximately .1 M in acid. The solution was then polarographed. By means of the above technique it was possible to follow reactions with half life of only a few seconds.

Polarography of Chromium Complexes

Figure 9 (53) shows a series of polarograms obtained during the hydrolysis of a solution of $\left[Cr(NH_3)_5 Br\right] (ClO_4)_2$

Figure 9

Polarograms[a] obtained during aquation of $[Cr(NH_3)_5Br](ClO_4)_2$ in 0.3M $HClO_4$ at 25°C

A. 3 mins.

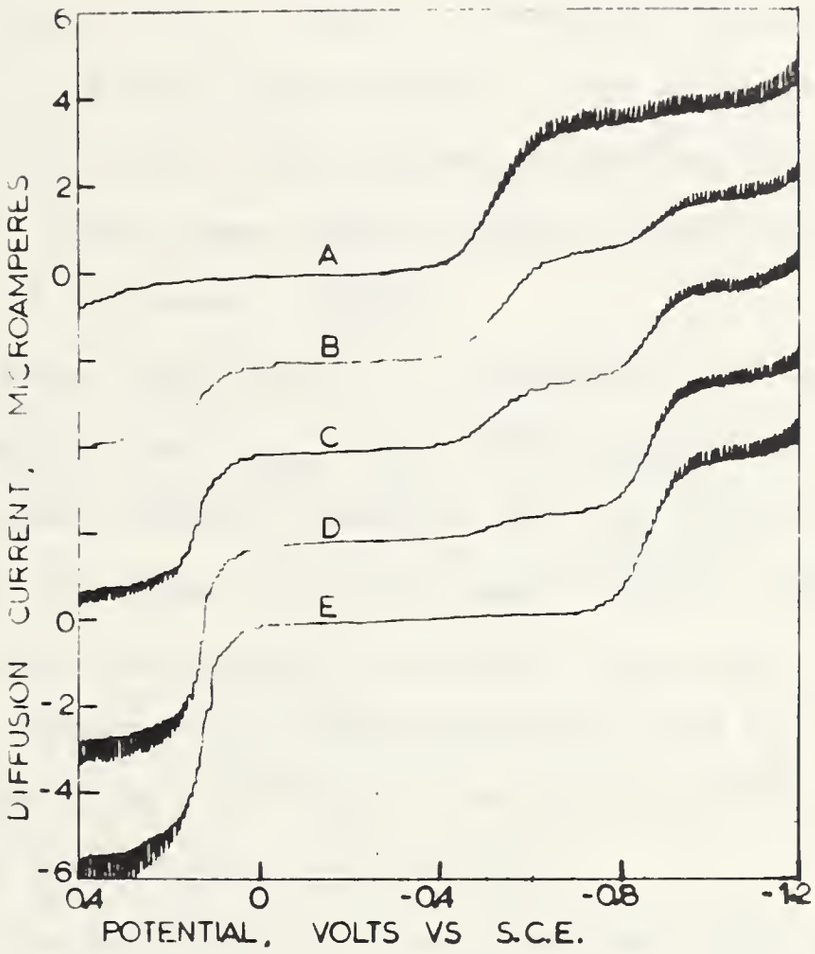
B. 60 mins.

C. 150 mins.

D. 300 mins.

E. Solution was heated

[a] Fig. 9 was obtained from Dr. W.E. Harris


6
4
2
0
0
-2
-4
-6
A
B
C
D
E
DIFFUSION CURRENT, MICROAMPERES
0.4
0
-0.4
-0.8
-1.2
POTENTIAL, VOLTS VS S.C.E.

in 0.3 M perchloric acid at 25°C. Initially, only the polarographic wave (at about -0.5V) is present, and this corresponds to the only electron reduction of $Cr(NH_3)_5Br^{++}$. As hydrolysis proceeds, two new polarographic waves appear, (fig. 9, B,C,D.) the one at +0.15 volts is the bromide oxidation wave and is as a result of bromide being released into the solution during the reaction. The second wave at about -0.9 volts is due to the one electron reduction of $Cr(NH_3)_5\ H_2O^{+++}$. Any one of these three waves could be used to follow the hydrolysis of the bromo complex.

When logarithm of i_d (diffusion current for the bromo complex) and $(i_{d_\infty} - i_{d_t})$ where i_{d_∞} is the diffusion current after complete reaction and i_{d_t} is the diffusion current at any time t for the aquo complex, were plotted against time, two parallel straight lines were obtained. The rate constants at 25°C calculated from the slopes of the curves were 6.25×10^{-3} min^{-1} and 6.10×10^{-3} min^{-1} for the bromo and aquo complex respectively.

The hydrolysis of the bromo and iodo complexes were studied by following the decrease in diffusion current due to the reduction of the bromo and iodo complexes respectively.

Fig. 10 shows sketches of the polarographic reduction waves of chloro, bromo, iodo and aquo complexes. It is apparent that the half wave potentials of the reduction wave, of both the bromo and iodo complexes are sufficiently different from the half wave potential of the aquo complex that the hydrolysis reaction can be studied by following the decrease in their diffusion currents.

It was therefore, possible to study the hydrolysis reaction at any pH without complications from subsequent reactions of the aquo complex.

Since the chloro and aquo complexes are reduced at very nearly the same potential, (C and D, fig. 10), it was not possible to use either of these reduction waves for following the hydrolysis of the chloro complex. However, by using $\left[Cr(NH_3)_5\ Cl\right]\ (ClO_4)_2$ salt, it was possible to follow the appearance of the chloride ion. The change in the diffusion current due to oxidation of liberated chloride ion was measured at +0.4 volts versus the saturated calomel electrode. This potential was selected because it corresponds to the potential of the chloride wave at its plateau. The potential was supplied by a saturated mercury, mercuric sulphate half cell.

The polarographic cell used was the same as was described earlier except that the saturated calomel electrode was replaced by the mercuric sulphate half cell.

The diffusion current was measured by short circuiting a Scalamp galvanometer between the sulphate half cell and the dropping mercury electrode according to a technique previously described (52).

Preliminary measurements were made with standard chloride solutions consisting of hydrochloric and perchloric acid mixtures. The concentration of the hydrochloric acid was varied with the perchloric acid added to keep the ionic strength constant at 0.1.

Figure 10.

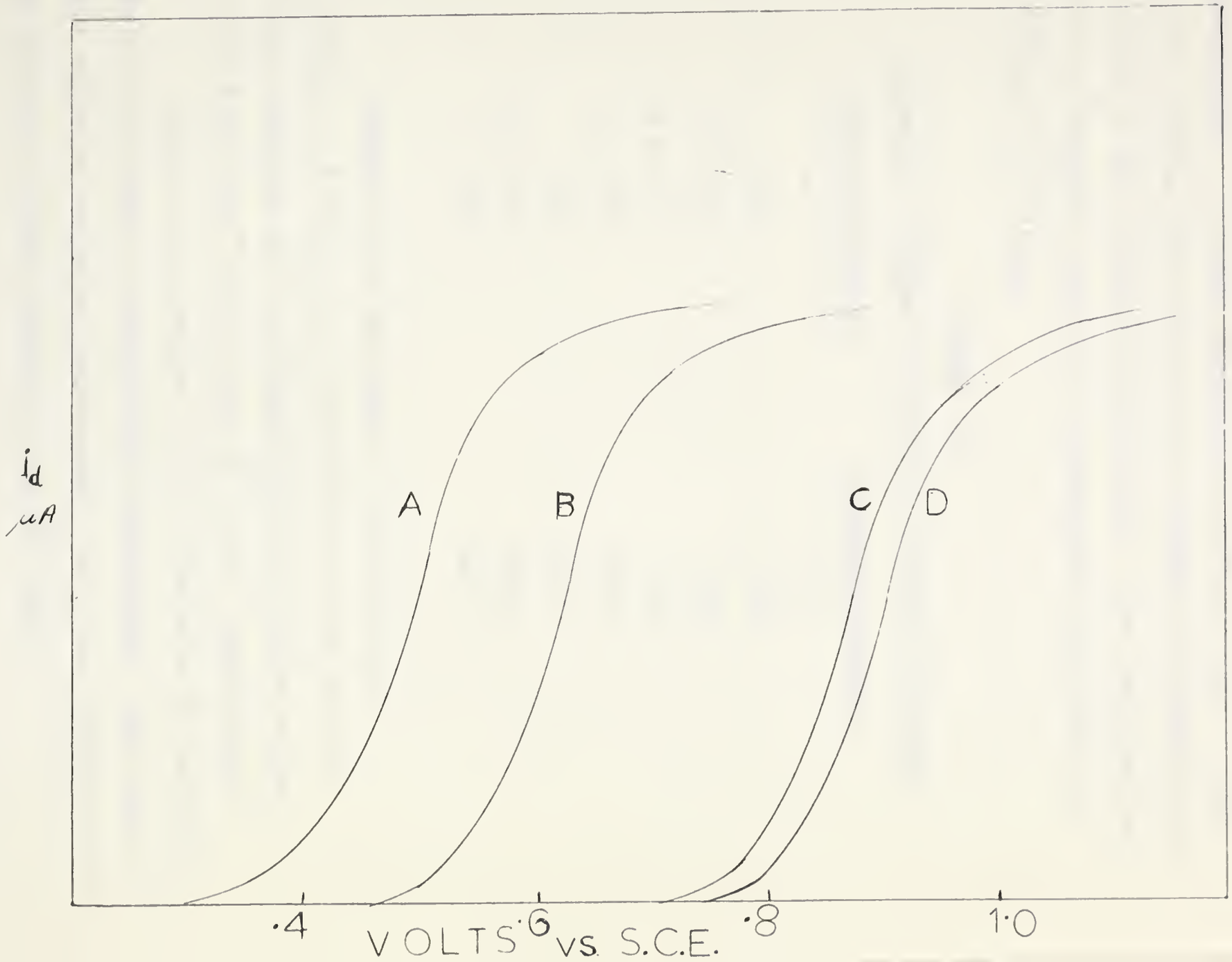
Sketch of the polarographic waves of the Halopentamminechromium (III) complexes in 0.1M perchloric acid

A. 10^{-3}M $Cr(NH_3)_5 I^{++}$

B. 10^{-3}M $Cr(NH_3)_5 Br^{++}$

C. 10^{-3}M $Cr(NH_3)_5 Cl^{++}$

D. 10^{-3}M $Cr(NH_3)_5 H_2O^{+++}$


i_d
μA
A
B
C
D
·4
·6
·8
1·0
VOLTS vs. S.C.E.

The diffusion current was then measured with the the electrolysis cell at $0^{o}C$, and plotted against chloride concentration. A linear relation, as shown in fig. 11, was obtained showing that the diffusion current is directly proportional to the chloride concentration. The technique described is therefore valid for following the hydrolysis of $\left[Cr(NH_3)_5\ Cl\right](ClO_4)_2$.

TABLE IV

DIFFUSION CURRENT IN STANDARD CHLORIDE SOLUTIONS

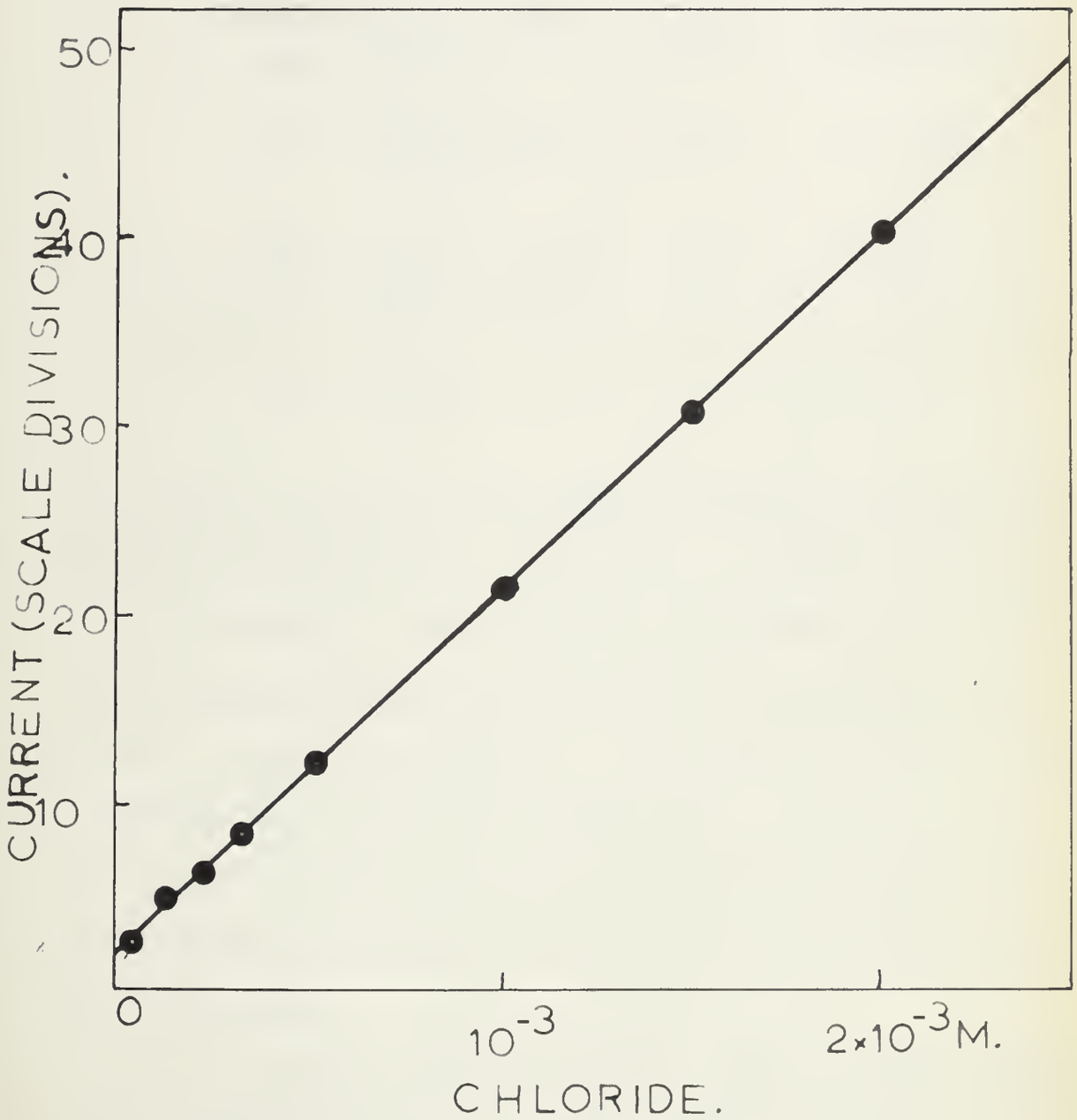
Chloride (Molar)	Diffusion Current
--	2.46
10^{-4}	4.98
2×10^{-4}	6.08
3×10^{-4}	8.30
5×10^{-4}	12.0
10^{-3}	21.1
1.5×10^{-3}	30.6
2×10^{-3}	40.1

Comparison of the rates of hydrolysis of $\left[Cr(NH_3)_5\ Cl\right](ClO_4)_2$ in 0.1M perchloric acid at $45^{o}C$ by this technique and spectrophotometrically gave values of $5.70 \times 10^{-3}\ min^{-1}$ and $5.78 \times 10^{-3}\ min^{-1}$ respectively.

Some of the studies on the hydrolysis of the chloro complex were made by conventional polarography. Here the complete chloride oxidation polarographic wave was obtained, and the diffusion current measured from the curve.

Figure 11

Plot of diffusion current against concentration for chloride ion.


50
40
30
20
10
CURRENT (SCALE DIVISIONS).
0
10^{-3}
2×10^{-3}M.
CHLORIDE.

Effect of added salts on the half wave potential of $Cr(NH_3)_5Br^{++}$

In table V are reported a few preliminary observations on the effect of added salts on the half wave potential of the bromopentamminechromium (III) complexes at 0^oC.

TABLE V

Added electrolyte	pH	$E_{1/2}$ (volts)
0.1M $HClO_4$		.63
0.1M (Pyridine perchlorate buffer)	6.0	no wave
.05 sodium citrate	6.6	1.005
.05 sodium succinate	6.6	.89
0.1M H_2SO_4		.75

The data in table V show that in the presence of various anions, the half wave potential is shifted to a more negative potential. This has been attributed to outer sphere or ion pair formation(71) between the complex, and the added anion. Since the chromium complexes reduction waves are irreversible (55), it has not been possible to correlate the shift in half wave potential to the magnitude of the equilibrium constant for the chromium complexes and a particular anion.

It was reported earlier that a better separation of the bromo and aquo waves were obtained in the presence of sulphate rather than perchlorate. In table VI are shown the values for the half wave potentials and diffusion currents for the bromo and aquopentamminechromium (III) in

presence of both perchlorate and sulphate.

In the presence of sulphate the half wave potentials of both aquo and bromo complex are shifted to a more negative potential, but the aquo more so than the bromo. This is believed to be due to the fact that the aquo complex due to its higher positive charge forms a stronger outer sphere complex than does the bromo complex, thus, the consequently greater shift in half wave potential.

TABLE VI

HALF WAVE POTENTIALS ($E_{1/2}$) AND DIFFUSION CURRENTS (I_d) FOR BOTH $Cr(NH_3)_5 Br^{++}$ AND $Cr(NH_3)_5 H_2O^{+++}$ IN PRESENCE OF SULPHATE AND PERCHLORATE AT 0°C.

	$Cr(NH_3)_5 Br^{++}$		$Cr(NH_3)_5 H_2O^{+++}$	
Added Electrolyte	$E_{1/2}$ (volts)	I_D μA	$E_{1/2}$ (volts)	I_D μA
0.1M $HClO_4$	.63	2.9	.85	3.0
0.1M H_2SO_4	.75	2.7	1.00	2.7

Determination of Rate Constant

For a first order reaction, the specific rate constant k can be expressed in the form of equation (XLII).

$$k = \frac{2.303}{t} \log \frac{c_o}{c} \qquad \text{(XLII)}$$

where c_o is the original concentration of the reactant and c the concentration of reactant at any time t. The measured diffusion currect as given by the Ilkovic equation (56) is proportional to the concentration of the complex being

reduced. Thus, the concentration at any time t will be proportional to the diffusion current.

$$k = \frac{2.303}{t} \log \frac{i_{d_o}}{i_{d_t}} \qquad \text{(XLIII)}$$

Where i_{d_o} is the diffusion current at zero time and i_{d_t} the diffusion current at any time t. For a first order reaction a plot of $-\log i_{d_t}$ against time should give a straight line. The rate constant is then calculated from the slope of the line and is given by equation (XLIV).

$$k = 2.303 \times \text{slope} \qquad \text{(XLIV)}$$

Fig. 12 shows a plot of $-\log i_d$ against time for the aquation of $Cr(NH_3)_5 Br^{++}$ at 25°C in presence of .0075 M sodium succinate.

TABLE VII

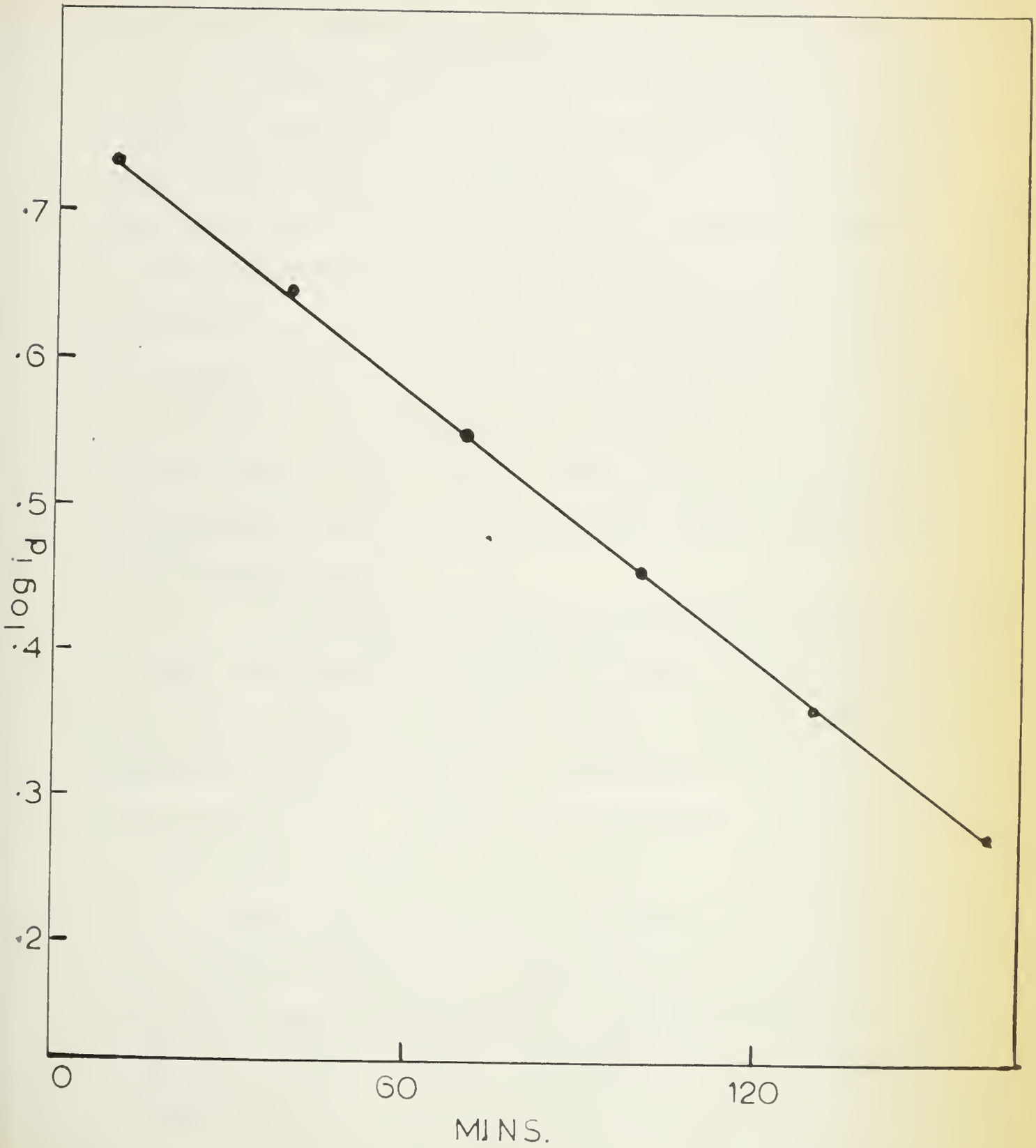
DIFFUSION CURRENT READINGS DURING THE HYDROLYSIS OF $Cr(NH_3)_5 Br^{++}$ AT 25° IN PRESENCE OF .0075 M SODIUM SUCCINATE

Time mins.	Diffusion Current (i_d) μA	log i_d
10	5.51	.735
40	4.46	.643
70	3.60	.548
100	2.92	.455
130	2.41	.369
160	1.96	.277

In the studies on the effect of anion on the aquation rate, when the anion concentration was below .005M, it was

Figure 12

Plot of log diffusion current against time for aquation of $Cr(NH_3)_5Br^{++}$ at 25°C in .0075M Sodium Succinate


·7
·6
·5
·4
·3
·2
log i_p
0
60
120
MINS.

found desirable to increase the buffer capacity of the solution by the addition of an ammonia-ammonium perchlorate buffer. In these cases, a pH of 8 was maintained by a buffer mixture whose ammonium perchlorate concentration was .01 M.

It was not possible to study the effect of sodium maleate and fumarate on the rate under the conditions described above, since both maleic and fumaric acid were reduced in the potential range of the chromium complexes. The reduction potentials of maleic and fumaric acid were dependent upon the pH of the solution, and by suitable control of pH, it was possible to change their reduction potentials to sufficiently more negative values that they did not interfere with the wave of the complex. The most convenient pHs for polarographic analysis of the fumarate and maleate were 6 and 8, respectively.

In solutions where the concentration of maleate and fumarate were higher than .005 M, the pH of the original solution containing the complex and the salt of the anion was adjusted to the required pH by addition of a very small amount of perchloric acid. Samples were withdrawn and polarographed as previously described, except that no acid was added.

When the concentration of maleate and fumarate were below .005 M, enough of the appropriate amine perchlorate buffer was added to the sample to be polarographed in order to give the desired pH and final perchlorate concentration of 0.1M.

III AQUATION REACTION

Experimental Results

The effect of pH on the aquation rate of both chloro and iodo complex was investigated over the entire pH range. The rates of reaction for the chloro and iodo complexes were investigated at 45°C and 0°C respectively. Since the iodo complex hydrolyses at a very fast rate, it was more convenient to follow the reaction at 0°C.

Figs. 13 and 14 show a plot of the pseudo-first order rate constant against pH for the chloro and iodo complexes respectively. The data for figs. 13 and 14 were taken from tables (VIII) and (IX) respectively.

For the intermediate pH range, the amine perchlorate buffers, given in table (I) were used. Since the rate was constant over the pH range 1 - 10, it was concluded that neither the free bases nor the cations associated with these buffers affected the hydrolysis reaction. For example, the result at pH 8 in fig. 13 was obtained from separate runs using 2 amino pyridine buffer in one and ammonia in the other.

On the basis of the pH dependence, the hydrolysis of the halopentamminechromium (III) complexes, can be divided into two portions. Figs. 13 and 14 and the data in tables (VIII) and (IX) illustrate that the reaction is pH independent over the pH range 1 - 10, with the rate being dependent only on the concentration of complex. The reaction occurring is the aquation reaction (XLV).

TABLE VIII

EFFECT OF pH ON THE RATE OF HYDROLYSIS OF CHLOROPENTAMMINECHROMIUM (III) ION AT 45°C

pH	$k \times 10^3 mins^{-1}$	log k
1	5.76	-2.24
2	5.80	-2.24
4	5.78	-2.24
7	5.80	-2.24
9.7	5.75	-2.24
10.25	6.46	-2.19
11.0	7.38	-2.13
11.4	13.5	-1.87
11.98	34.7	-1.46
12.28	68.5	-1.16
12.98	208	- .681
13.28	290	- .538
13.98	820	- .087

TABLE IX

EFFECT OF pH ON THE HYDROLYSIS RATE OF IODOPENTAMMINECHROMIUM (III) ION AT $0^{o}C$.

pH	$k \times 10^{3} mins^{-1}$	log k
2.0	2.41	-2.62
6.0	2.43	-2.616
9.0	2.48	-2.610
10.0	3.07	-2.513
12.0	48.3	-1.32
13.0	244	- .613

Figure 13

Effect of pH on the rate constant for hydrolysis of $Cr(NH_3)_5Cl^{++}$ at 45.0°C.

All solutions were 0.1M in perchlorate except at pH 14. The open circle at pH 14 represents the data corrected for additional electrolyte necessarily present.

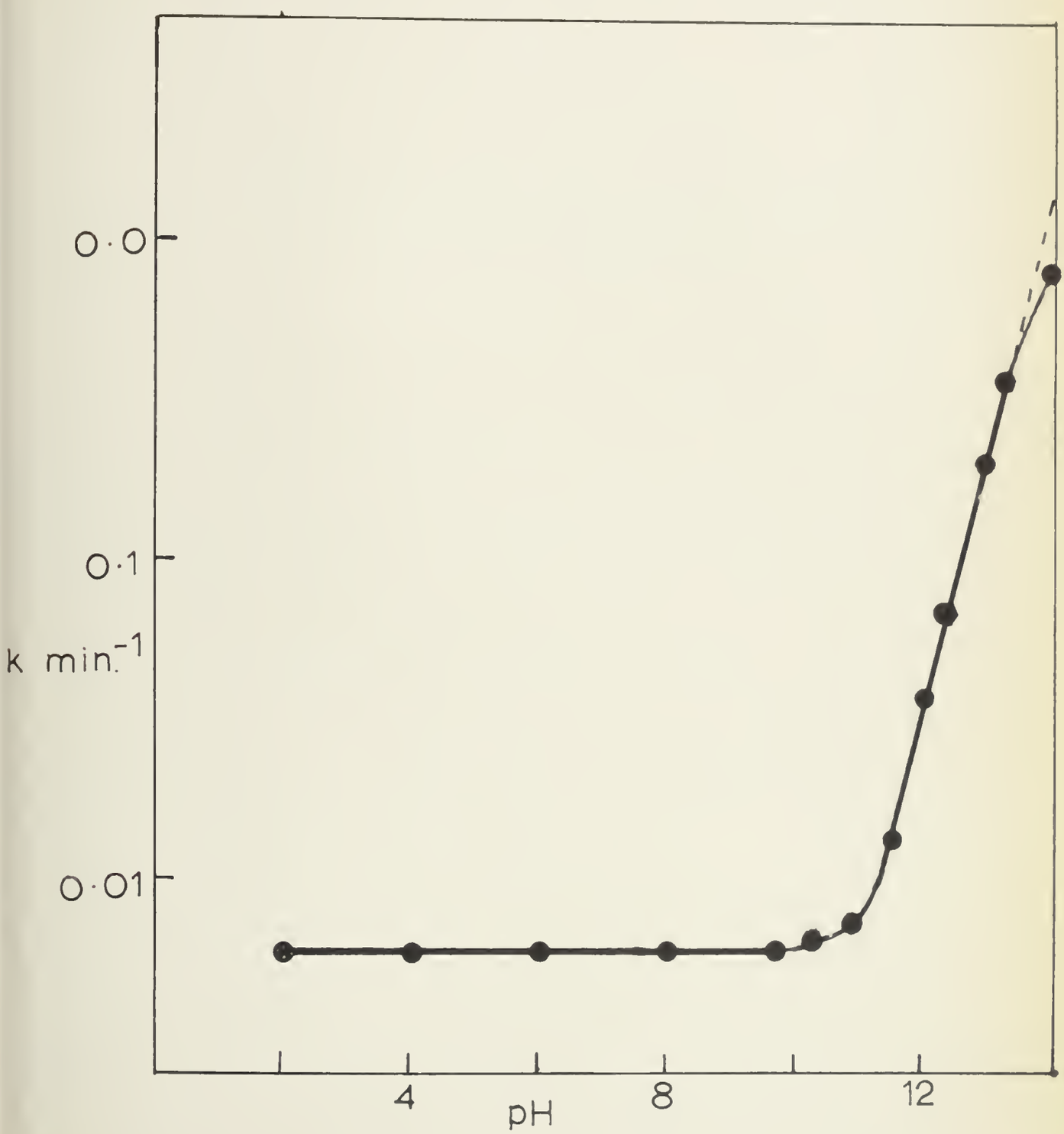
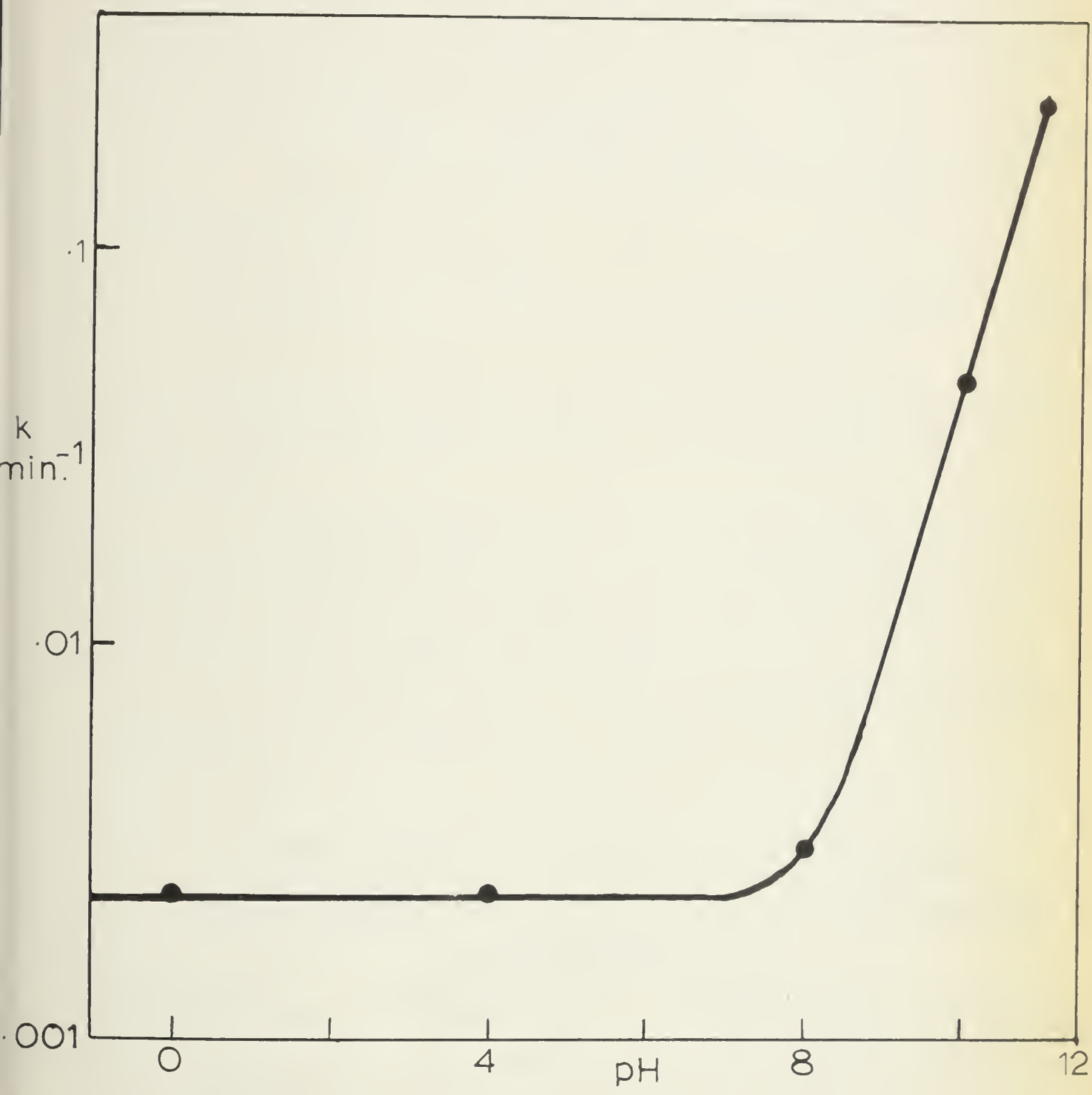

0·0
0·1
k min.$^{-1}$
0·01
4
8
12
pH

Figure 14

Effect of pH on the rate of hydrolysis of $Cr(NH_3)_5I^{++}$ at 0.0°C.

All solutions were 0.1M in perchlorate


·1
k
min.⁻¹
·01
·001
0
4
pH
8
12

$$Cr(NH_3)_5 X^{++} + H_2O \longrightarrow Cr(NH_3)_5 H_2O^{+++} + X^- \quad \text{(XLV)}$$

Where X is chloride, bromide, or iodide.

Above a pH of 11.5, the rate is linearly dependent upon the hydroxide concentration, and obeys the second order rate law, shown in equation (XLVI).

$$\text{Rate} = k \left[\text{complex}\right]^{++} \left[OH\right]^{-} \quad \text{(XLVI)}$$

This reaction has been referred to as the base hydrolysis (57).

$$Cr(NH_3)_5 X^{++} + OH^- \longrightarrow Cr(NH_3)_5 OH^{++} + X^- \quad \text{(XLVII)}$$

In the pH region 10 to 11.5, both aquation and base hydrolysis contribute significantly to the observed rate of reaction.

The pH dependence of the hydrolysis of both chloro and iodo complexes, are in agreement with that reported earlier for the bromo complex (58).

The data of table X show that the rates of aquation increase in the order chloro < bromo < iodo.

TABLE X

RATE CONSTANTS FOR AQUATION OF THE HALOPENTAMMINECHROMIUM (III) IONS AT LOW pH IN .01M PERCHLORIC ACID SOLUTIONS AT 25°C

Reactant	$Cr(NH_3)_5 Cl^{++}$	$Cr(NH_3)_5 Br^{++}$	$Cr(NH_3)_5 I^{++}$
k_1 (pH 1-10 min^{-1}	5.6×10^{-4}	6.2×10^{-3}	7.3×10^{-2}
k_1 min^{-1}(a) previous work	5.8×10^{-4}	3×10^{-3}	10^{-2} (b)

(a) Ref. 59

(b) 0.0°

The effect of changing the concentration of the complex on the aquation rate is shown in table XI.

TABLE XI

RATE CONSTANT FOR THE AQUATION OF $Cr(NH_3)_5Cl^{++}$ AS A FUNCTION OF CONCENTRATION OF THE COMPLEX AT 25.0°C

Complex (molar) Concentration	$k_1 \times 10^4$ [(a)] min^{-1} in 0.1 M $HClO_4$
10^{-3}	5.7
3×10^{-3}	5.6
10^{-2}	5.6

(a) Rates were followed spectrophotometrically.

The rate constant was substantially independent of the initial concentration of chromium. Selbin and Bailar (29) observed that the concentration of complex in solution affected the rate of aquation of cis dichlorobis (ethylenediamine) chromium (III) complex.

The rates of aquation for the three halo complexes were measured as a function of temperature.

TABLE XII

RATE CONSTANTS FOR THE AQUATION OF HALOPENTAMMINE-CHROMIUM (III) IONS AS A FUNCTION OF TEMPERATURE $k \times 10^3 min^{-1}$

Reactant T	$1/T \times 10^3$	$Cr(NH_3)_5 Cl^{++}$ k	$Cr(NH_3)_5 Br^{++}$ k	$Cr(NH_3)_5 I^{++}$ k
0°	3.66	.018	.193	2.25
9°	3.55	--	--	8.05
15°	3.47	.143	1.70	19.0
30°	3.30	1.05	11.7	12.6
45°	3.15	5.6	66.1	too fast
60°	3.00	30.1	--	--

Fig. 15 shows plots of the pseudo-first order rate constant against the reciprocal of the absolute temperature. Activation energies, frequency factors and entropies of activation calculated from the slopes of the lines are given in table (XIII).

TABLE XIII

ACTIVATION ENERGIES, FREQUENCY FACTORS AND ENTROPIES OF ACTIVATION FOR THE AQUATION OF HALOPENTAMMINE-CHROMIUM (III) IONS IN 0.1M PERCHLORATE SOLUTIONS

Reactant	$Cr(NH_3)_5 Cl^{++}$	$Cr(NH_3)_5 Br^{++}$	$Cr(NH_3)_5 Z^{++}$
Activation Energy pH 1-10 k cal.	22.4	22.3	22.1
Frequency Factor pH 1-10 min^{-1}	1×10^{13}	1.6×10^{14}	1.3×10^{15}
Entropy of Activation (entropy units)	1.3	5.8	9.9

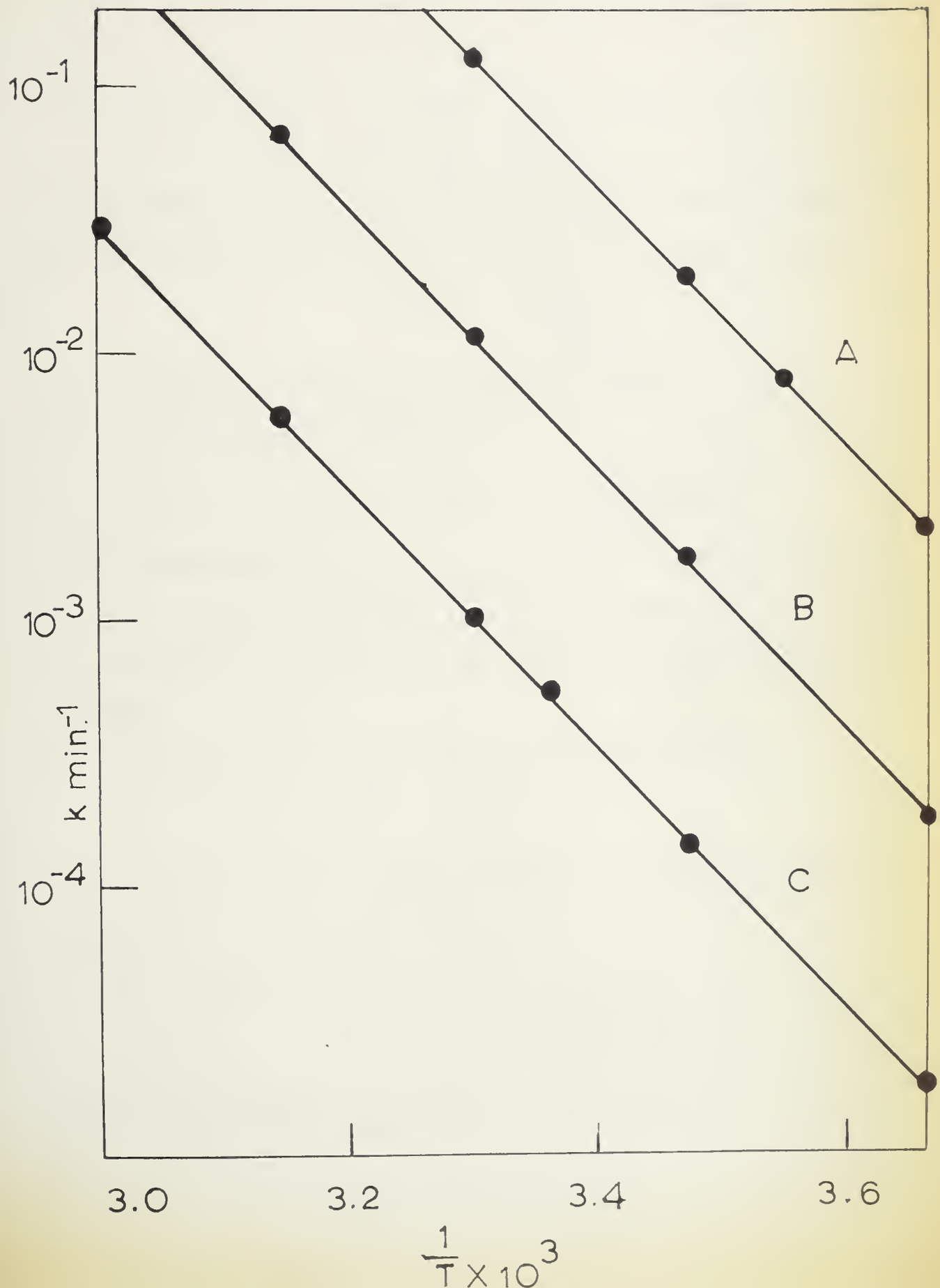
Figure 15

Effect of temperature on the rate of aquation of the three halopentamminechromium (III) complexes in .01M $HClO_4$

A. $[Cr(NH_3)_5 I] I_2$

B. $[Cr(NH_3)_5 Br] Br_2$

C. $[Cr(NH_3)_5 Cl] (ClO_4)_2$


10^{-1}
10^{-2}
10^{-3}
10^{-4}
k min.$^{-1}$
A
B
C
3.0
3.2
3.4
3.6
$\frac{1}{T} \times 10^3$

Activation energies and frequency factors were calculated from the rate data as follows:

The Arrhenius equation was obeyed by all three halo complexes.

$$k = Z \cdot e^{-E_a/RT}$$

where k is the rate constant, Z the frequency factor, E_a the activation energy, R the gas constant and T the absolute temperature. The slope of the straight line obtained from a plot of log k against 1/T is given in equation (XLIX)

$$\text{slope} = \frac{E_a}{2.303R} \qquad \text{(XLIX)}$$

E_a (activation energy) = slope x 2.303 R.

From the Arrhenius equation (L)

$$\log Z = \log k + \frac{E_a}{2.303\ RT} \qquad \text{(L)}$$

By substituting values for E_a, R and T, into the equation (L), the frequency factor Z can be calculated. The entropy of activation (ΔS) can be evaluated from the rate data as follows:

The free energy of activation ΔF is defined by:

$$\Delta F^{\neq} = -RT \ln K^{\neq} \qquad \text{(LI)}$$

where $K^{\neq}$ is an equilibrium constant for the formation of the transition state or activated complex.

The heat of activation is defined by:

$$\Delta H^{\neq} = RT^2 \frac{d \ln K_p^{\neq}}{dT} \qquad \text{(LII)}$$

where $K_p^{\neq}$ is $K^{\neq}$ but in pressure units.

$$K_p^{\neq} = K_c^{\neq} (RT)^{1-n} \qquad \text{(LIII)}$$

where K_c is concentration equilibrium and n is the molecularity of the reaction.

$$\Delta S^{\ddagger} = \frac{\Delta H^{\ddagger} - \Delta F^{\ddagger}}{T} \qquad \text{(LIV)}$$

By substituting into equation (LI) for $\Delta F^{\ddagger}$ equation (LV) is obtained.

$$K = e^{-\Delta S/R} \cdot e^{-\Delta H^{\ddagger}/RT} \qquad \text{(LV)}$$

From the transition state theory treatment of reaction rates (10), the rate of reaction is given by:

$$k_r = \left(\frac{kT}{h}\right) \cdot K^{\ddagger} \qquad \text{(LVI)}$$

where $\frac{kT}{h}$ is called the universal frequency factor, k being the Boltzman constant, h Planck's constant, and T the absolute temperature. Substitution for K from equation (LV) gives equation (LVII).

$$k_r = \frac{kT}{h} e^{\Delta S^{\ddagger}/R} \cdot e^{-E_0/RT} \qquad \text{(LVII)}$$

$\Delta S^{\ddagger}$ is independent of the standard states (since it is only the change in entropy that is measured) and can be calculated from equation (LVII) by substituting in values for the activation energy rate constant and temperature. The entropy of activation $\Delta S^{\ddagger}$, represents the total change in entropy of the reactants and solvent, on formation of the transition state.

The data in table X show that the rate constants for the aquation of the halo complexes, increase as the leaving group is varied from chloride to bromide to iodide. The data in table XIV give a comparison of the aquation rates for the halo complexes of both cobalt (III) and chromium (III).

TABLE XIV

RATE CONSTANTS FOR THE AQUATION OF HALOPENAMMINE COMPLEXES OF COBALT (III) AND CHROMIUM (III) AT 25°C

X^-	$Co(NH_3)_5X^{++}$ k min^{-1}	$Cr(NH_3)_5X^{++}$
Cl	1.0×10^{-4} (a)	5.6×10^{-4}
Br	3.8×10^{-4} (a)	6.2×10^{-3}
I	5×10^{-4} (a)	7.3×10^{-2}
$\frac{k_{Br}}{k_{Cl}}$	3.8	11.0
$\frac{k_I}{k_{Br}}$	1.3	11.7

(a) Ref. 61.

Discussion

The data in table (XIV) show that the chromium (III) complexes aquate at a faster rate than do the corresponding cobalt (III) complexes. The rate of aquation of cobalt(III) complexes is only slightly dependent on the nature of the metal halogen bond, whilst for the chromium complexes, the rate shows a greater than 100 fold increase, when the leaving group is varied from chloride to iodide. This great difference in rate for the three halopentammine-chromium (III) complexes, would suggest that the aquation reaction is more dependent upon the strength of the metal halogen link in the case of chromium (III) than of cobalt (III). This would, in turn, suggest that the rate determining step is less likely to be SN_2 lim in the case of

in the case of chromium (III) than of cobalt (III). The strong dependence of the rate on the nature of the chromium halogen bond may even be indicative of an SN_1 mechanism, with the rate determining step being the formation of a five co-ordinate intermediate, as shown in equation (LVIII)

$$Cr(NH_3)_5 X^{++} \xrightarrow{slow} Cr(NH_3)_5^{+++} + X^- \qquad \text{(LVIII)}$$

$$Cr(NH_3)_5^{+++} + H_2O \xrightarrow{fast} Cr(NH_3)_5 H_2O^{+++} \qquad \text{(LIX)}$$

If this is the mechanism, then the observation that the activation energies of the reaction is essentially independent of the halide being removed is surprising. This observation has been reported earlier by A. Vlcek (62). From the data in tables (VII) and (IX), it appears that the variation in rate, as the nature of the leaving group is changed, originates in the frequency factors, and not in the activation energies. The change in the frequency factor could be attributed to a difference in the entropy of activation, shown in table XIII. The increase in rate, in going from chloro to bromo to iodo complex, is thus a result of a more favourable entropy of activation. Consequently, the original argument against an SN_2 mechanism is not valid. Nevertheless, it is surprising that there is no difference in activation energy among these three complexes. In an effort to rationalize this observation, it is desirable to consider the energy terms that might be applicable to this set of reactions. For the aquation reaction there will be seven principal energy terms to be considered.

1) Bond rupture.

2) Bond formation e.g. specific interaction of a solvent molecule with metal ion of the complex.

3) Solvation of the reactant complex ion.

4) Solvation of the entering solvent molecule.

5) Solvation of the product complex anion.

6) Solvation of the product anion.

7) Energy necessary to reorganise the ion to produce the transition state.

For the aquation reaction the only terms that are likely to differ significantly when X is varied from chloride to bromide to iodide are (1) and (6). The other terms (2), (3), (4), (5) and (7), would not be expected to differ significantly as X is varied. The anion solvation energy and the bond rupture energy have not been measured for the chromium (III) complexes but the values which have been estimated for manganese (II), an analogous ion, are shown in table XV for the reaction shown in equation (LX).

$$Mn\,X^{+} \longrightarrow Mn^{++} + X^{-} \qquad \text{(LX)}$$

The data in table XV show that the rupture of the MnX bond where X is Br, Cl or I, does not depend on the strength of the bond, when carried out in aqueous solution. This is reflected in the approximate constancy of E_D-E_S. It appears that solvation of the anion compensates for the difference in bond strength through the sequence, chloride to bromide to iodide. This kind of phenomenon is also reflected

TABLE XV

ENERGY TERMS CONTRIBUTING TO BOND RUPTURE IN MnX

Anion	Anion Solvation Energy $(E_S)^a$ k cal	Energy of bond rupture $(E_D)^b$ k cal	$E_D - E_S$
F	-122.6	152	29
Cl	-88.7	146	57
Br	-81.4	141	60
I	-72.1	129	57

a) Ref. 63

b) Bond dissociation energies from T.L. Cottrell, "The Strength of Chemical Bonds", Butterworths Scientific Publication, London 1954; ionization potentials and electron affinities from T. Moeller, "Inorganic Chemistry", John Wiley and Sons, New York, 1952.

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in the values of the entropy of dissociation of the complexes $CrCl_2^+$, $Cr\ Br_2^+$ and $Zn\ Cl^+$, $Zn\ Br^+$, $Zn\ I^+$ in aqueous solution, as compiled by Bjerrum Schwarzenbach and Sillen (46). The enthalpies for dissociation of the chloro and bromochromium (III) complexes are 10.1 and 11.6 k cal, and for each of the zinc complexes, 0.0 k cal. It is therefore not surprising that the activation energies for the aquation of the halopentamminechromium (III) complexes are independent of the halogen being removed, since the decrease in bond energy in going from chloride to bromide to iodide, is likely to be compensated by the increase in anion solvation energy. This

argument would indicate that the solvent (in this case water) is directly involved in the transition state. As mentioned earlier (table X), the difference in rate, as the leaving group is changed from chloride to bromide to iodide, can be attributed to the variation in the entropy of activation. A study of gas phase entropies of bond ruptures, show an insignificant variation as the breaking bond varies from chloro to bromo to iodo (65). This would indicate that the observed changes in entropy of activation are not primarily due to the rupture of the chromium halogen bond. The other possibilty is that the difference in entropy of activation, originates from the effect of the halide on the transition state. Since the transition state for the aquation reaction involves separation of charges, it will be accompanied by reorientation of the solvent sheath around the reacting complex. The degree of re-orientation will be associated with the leaving group, since this is the only variable within the system. If the difference in entropy of activation is associated with the re-orientation of the solvent molecules around the complex, then the observed difference in entropy of activation ought to parallel, roughly, the thermodynamic entropies of the reaction.

Latimer and Jolly (63) have suggested a procedure for estimating the thermodynamic entropy of any reaction of this general form. The aquation reaction can be written as shown in equation (LXI).

$$\text{Halogen (bound)} + H_2O \longrightarrow H_2O_{(bound)} + \text{halogen (aq)} \qquad \text{(XVII)}$$

The change in entropy associated with the cation $Cr(NH_3)_5X^{++}$ can be assumed to be the same for all three, as the entropy of formation in the gaseous phase should be almost the same for all three halo complexes. The observed change in entropy, in going from chloro to bromo to iodo complex, is thus, a rough estimate of the thermodynamic entropy change for reaction (LXI). The various entropy terms in equation (LXI) have been reported (66). They are 9.4 eu. for bound water, 16.7 for free water, and 9 for bound bromide. These give a value of +4.7 eu. for ΔS. When similar calculations were applied to the chloro and iodo complexes the ΔS values were +0.8 and 7.2 eu. respectively. These values have approximately the same relationship to one another as do the entropies of activation for the aquation reaction, (i.e. 1.3, 5.8 and 9.9 given in table XIII for the chloro, bromo and iodo complexes respectively).

Since the activation entropies of the aquation reaction closely parallel the entropy change of reaction XVII it can be said that the difference in the activation entropies for the aquation reaction when the leaving group is varied from chloride to bromide to iodide is a result of the difference in the solvation energy associated with the released halogen. This would indicate that the solvent sheath is a direct participant in the aquation reaction. Since it is not possible to determine whether a specific water molecule

is involved in the transition state of the aquation reaction assignment of an SN_1 or SN_2 mechanism to the reaction becomes difficult.

It is suggested that the name "solvent assisted SN_1" best describes the mechanism of the aquation reaction.

IV SALT EFFECTS ON THE AQUATION REACTION

Experimental Results

The effect exerted by perchlorate ion upon the aquation rate of chloro, bromo and iodo complexes are shown in fig. 16. The linear dependence of rate upon concentration of salt is evident from the data.

TABLE XVI

EFFECT OF PERCHLORATE SALT UPON THE RATE OF AQUATION OF THE THREE HALOCOMPLEXES

Reactant	$k_1 \times 10^3$ min^{-1} $Cr(NH_3)_5Cl^{++}$ at 45°	$Cr(NH_3)_5Br^{++}$	$Cr(NH_3)_5I^{++}$
$NaClO_4$(molar)			
—	5.78	6.30	6.20
.01	5.82	6.25	-
.05	-	-	6.20
.1	5.70	6.20	-
.3	5.45	-	-
.5	5.25	-	5.72
.8	4.78	-	-
.9	-	5.27[a]	-
1.0	4.3	5.21[a]	5.18

[a] Data obtained from Dr. W. E. Harris

Figure 16

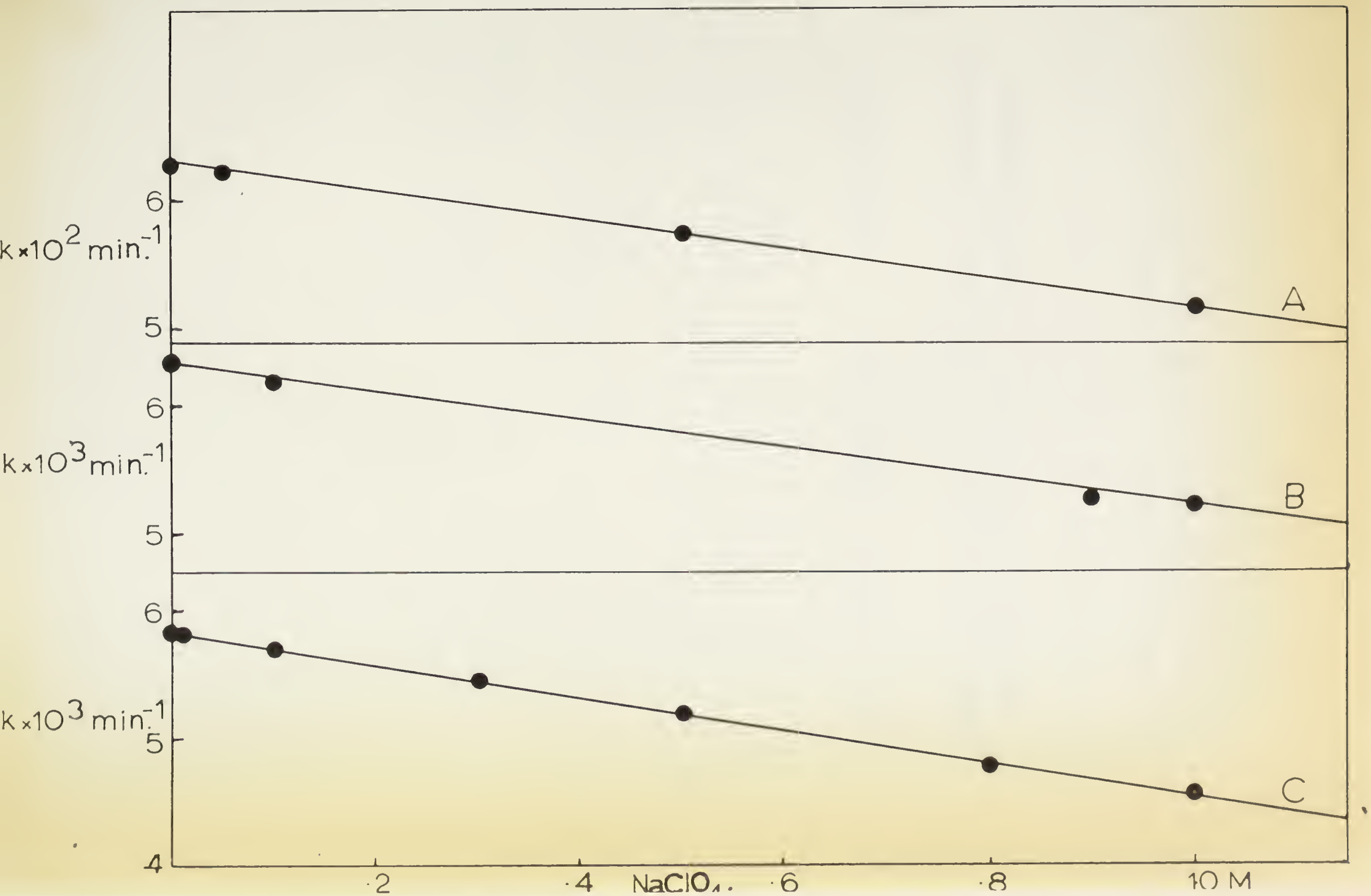
EFFECT OF SODIUM PERCHLORATE ON THE RATE OF AQUATION OF $Cr(NH_3)_5X^{2+}$

A. $Cr(NH_3)_5I^{2+}$ .001M at 25°C

B. $Cr(NH_3)_5Br^{2+}$ .001M at 25.3°C

data obtained from Dr. W. E. Harris

C. $Cr(NH_3)_5Cl^{2+}$ .02M at 45°C.


k×10² min.⁻¹
6
5
A
k×10³ min.⁻¹
6
5
B
k×10³ min.⁻¹
6
5
4
C
·2
·4
NaClO₄.
·6
·8
10 M

Perchlorate ion exerts the same mild retarding effect, irrespective of the chromium complex investigated. The data in Table XVII show that the effect of perchlorate is independent of the cation associated with the salt.

TABLE XVII

EFFECT OF DIFFERENT PERCHLORATE IONS ON THE RATE OF AQUATION OF CHLOROPENTAMMINE CHROMIUM (III) COMPLEX AT 45.0° C

Reactant added	Perchlorate Concentration	$k_1 \times 10^3$ min^{-1}
.3M $NaClO_4$	0.3M	5.45
.2 $NaCO_4$, .1M $HClO_4$	0.3M	5.40
.2 $LiClO_4$, .1M $HClO_4$	0.3M	5.35
.5M $NaClO_4$	0.5M	5.25
.4M $NaCO_4$, .1M $HClO_4$	0.5M	5.00
.4M $LiClO_4$, .1M $HClO_4$	0.5M	5.03
1.0M $NaClO_4$	1.0M	4.30
.9 $NaClO_4$, .1M $HClO_4$	1.0M	4.32
.9 $LiClO_4$, .1M $HClO_4$	1.0M	4.20

The effect exerted on the rate of aquation of both bromo and chloro complexes by other monovalent anions are shown in fig. 17 and Tables XVIII to XXI.

TABLE XVIII

EFFECT OF SODIUM ACETATE ON AQUATION OF $Cr(NH_3)_5Br^{++}$ at 25°C.

Acetate Concentration	$k \times 10^3$ min^{-1}
-	6.30
1×10^{-2}	6.35
5×10^{-2}	6.42
1×10^{-1}	6.50

TABLE XIX

EFFECT OF SODIUM BENZOATE ON AQUATION OF $Cr(NH_3)_5Br^{++}$ at 25°C.

Benzoate Concentration	$k \times 10^3$ min^{-1}
-	6.30
1×10^{-2}	6.45
6×10^{-2}	6.90
1×10^{-1}	7.25
3×10^{-2}	6.75
4×10^{-1}	8.05

TABLE XIX

EFFECT OF CHLORIDE, BROMIDE, IODIDE AND NITRATE ON RATE OF AQUATION OF $Cr(NH_3)_5Br^{++}$ at 25.0°C.

Salt	Concentration	$k \times 10^3$ min^{-1}
Chloride	2×10^{-2}	6.11
	1×10^{-1}	6.22
Bromide	5×10^{-2}	6.30
	1×10^{-1}	6.19
Iodide	1×10^{-1}	5.79
	1×10^{-1}	5.90
Nitrate	1×10^{-1}	6.20

TABLE XXI

EFFECT OF CHLORIDE ON AQUATION RATE OF $Cr(NH_3)_5Cl^{++}$ at 45.0°C.

Chloride[a]	$k \times 10^3$ min^{-1}
-	5.90
3×10^{-1}	5.85
4×10^{-1}	5.80
7×10^{-1}	5.95
1.05	6.05

[a] All solutions .02M in $HClO_4$

Figure 17

EFFECT OF MONOVALENT ANIONS UPON THE RATE OF AQUATION OF $Cr(NH_3)_5Br^{++}$ (upper curves) AT 25°C AND $Cr(NH_3)_5Cl^{++}$ (lower curves) AT 45°C

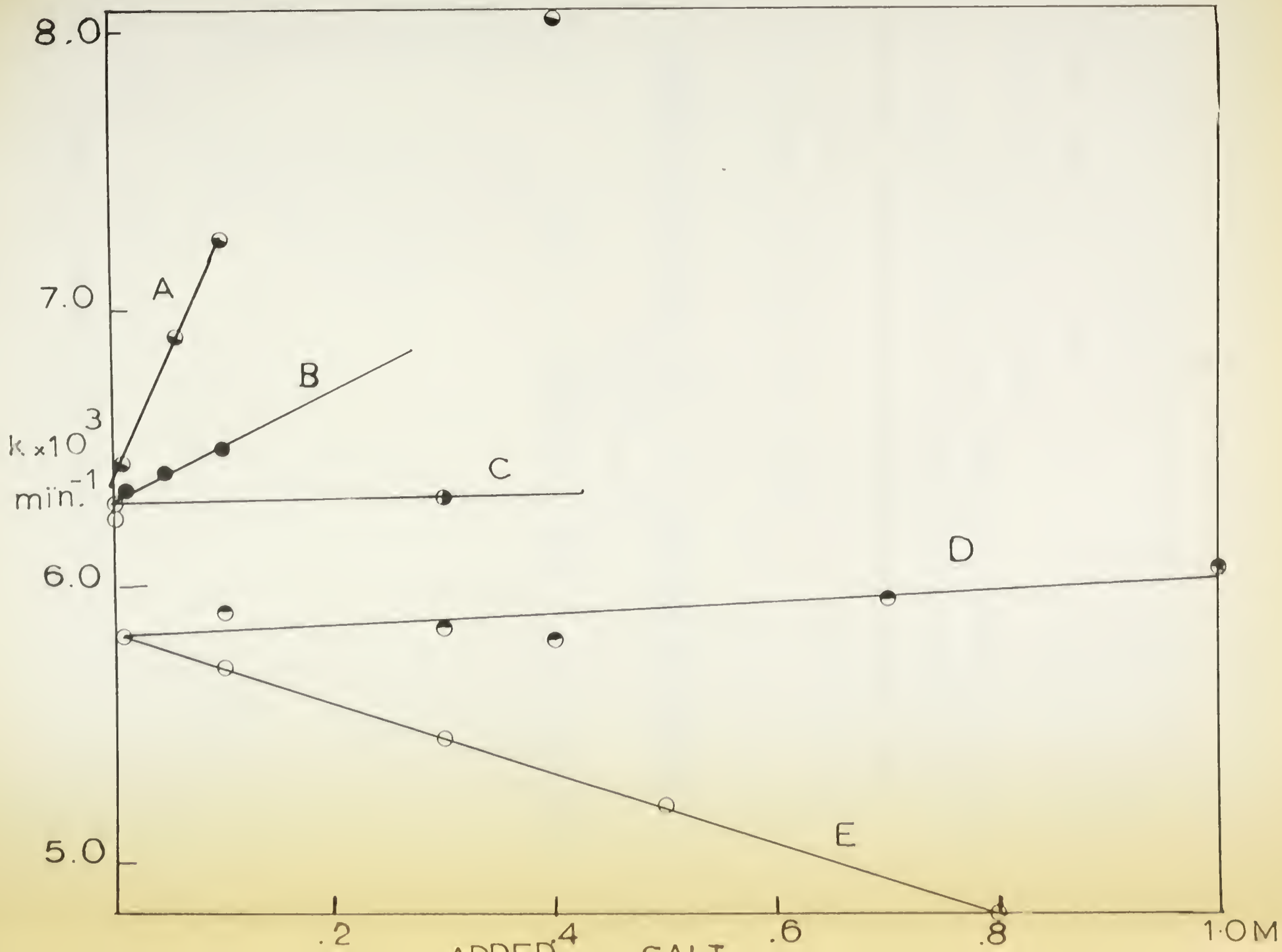
A. ◐ Sodium benzoate

B. ● Sodium acetate

C. ◑ Sodium bromide

D. ◒ Sodium chloride

E. ○ Sodium perchlorate


8.0
7.0
6.0
5.0
k x10^3
min.^-1
A
B
C
D
E
.2
.4
.6
.8
1·0M

The data for the effect of perchlorate on the rate of aquation of the chloro complex were given in Table XVI. From fig. 17, it is apparent that the rate is linearly dependent upon the salt concentration. The marked variation of the influence of different salts, is conveniently reported in terms of the fractional increase in rate produced by 0.1M electrolyte.

This will be the pseudo first order rate constant at .01M salt concentration divided by the pseudo first order rate constant at zero concentration of salt. The fractional increase in rate calculated from the data of fig. 17 are reported in Table XXII.

TABLE XXII

EFFECT OF MONOVALENT SALTS UPON THE RATE OF AQUATION OF $Cr(NH_3)_5X^{++}$

X^a	Salt	Fractional Increase $\frac{k_{.01}}{k_0}$	$k_{.01}$ x 10^3 min^{-1}
Cl^a	NaCl	1.00	5.82
Cl^a	$NaClO_4$	.97	5.80
Br^b	Na benzoate	1.15	6.32
Br^b	Na acetate	1.03	6.28
Br^b	$NaClO_4$	.98	
Br^b	NaBr	1.0	6.21
I^b	$NaClO_4$	1.02	6.28

[a] 45°C [b] 25°C

k_0 is the rate constant in .01M perchloric acid

Of the monovalent anions studied, sodium benzoate had the greatest influence on the aquation rate. The effect of a number of polyvalent anions on the aquation rate of $Cr(NH_3)_5Br^{++}$ are reported in Tables XXIII to XXXI.

Plots of the rate constant against the concentration of added salt are given in figs. 18, 19. For comparison purposes included in these figures are also the curves for the monovalent ions from fig. 17.

In fig. 21 are shown typical rate plots in the presence of three different citrate concentrations. The reaction follows a linear first order plot at all three concentrations of citrate.

Figure 18

PLOT OF THE PSEUDO FIRST ORDER RATE CONSTANT FOR THE AQUATION OF $Cr(NH_3)_5Br^{++}$ AT 25°C AGAINST CONCENTRATION OF ADDED ANIONS

A	●	Sodium citrate
B	◑	Sodium sulphate
C	◐	Sodium malonate
D	○	Sodium oxalate
E	⊘	Sodium succinate
F	⊗	Sodium acetate
G	⦶	Sodium perchlorate

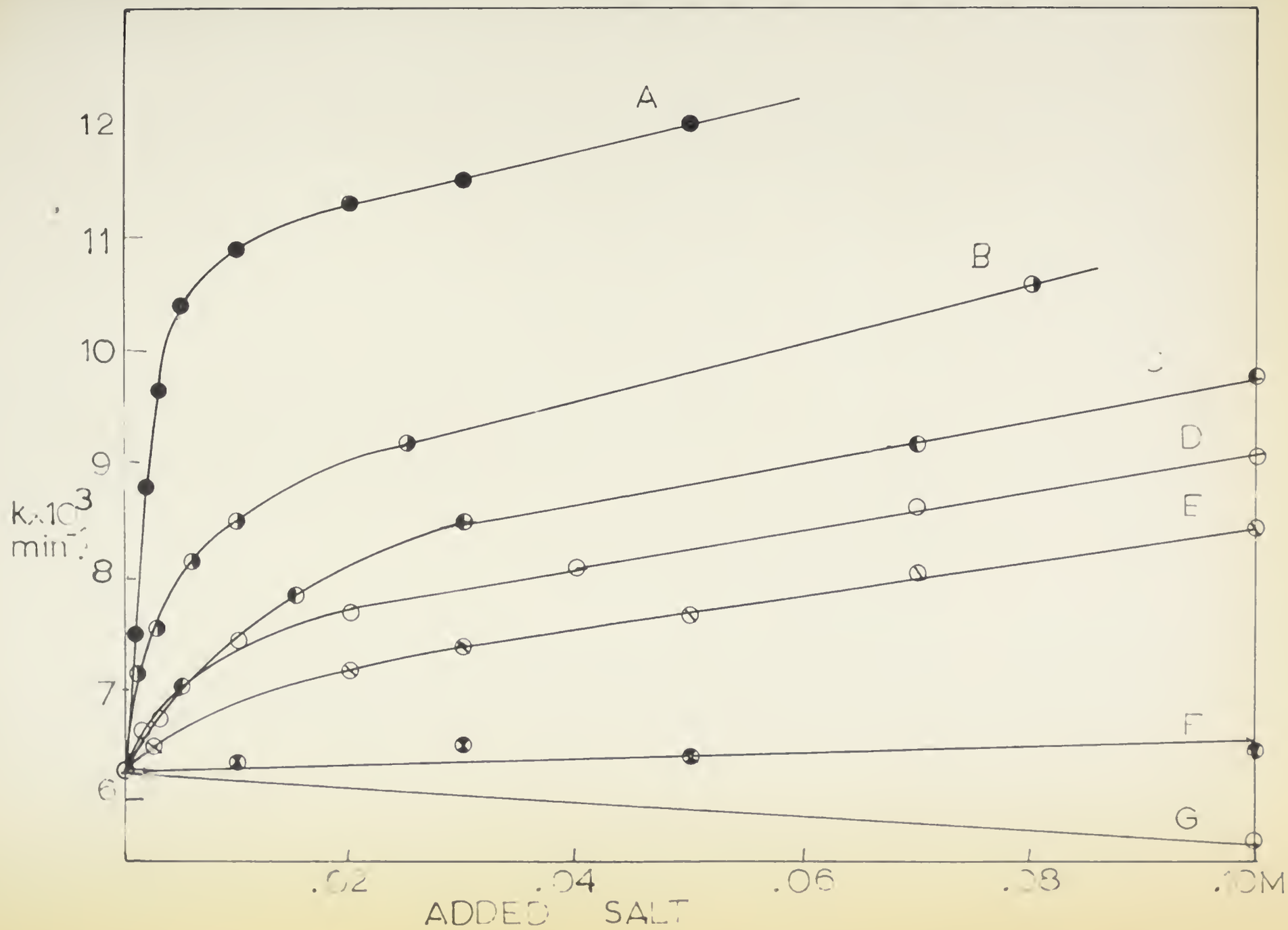

A
B
C
D
E
F
G
12
11
10
9
8
7
6
k×10³
min⁻¹
.02
.04
.06
.08
.10M
ADDED SALT

Figure 19

PLOT OF THE PSEUDO FIRST ORDER RATE CONSTANT FOR THE AQUATION OF $Cr(NH_3)_5Br$ AT 25°C AGAINST CONCENTRATION OF ADDED ANION

H	◑	Sodium maleate
I	◐	Sodium o-pthalate
J	⊘	Sodium fumarate
K	●	Sodium p-pthalate
L	○	Sodium benzoate

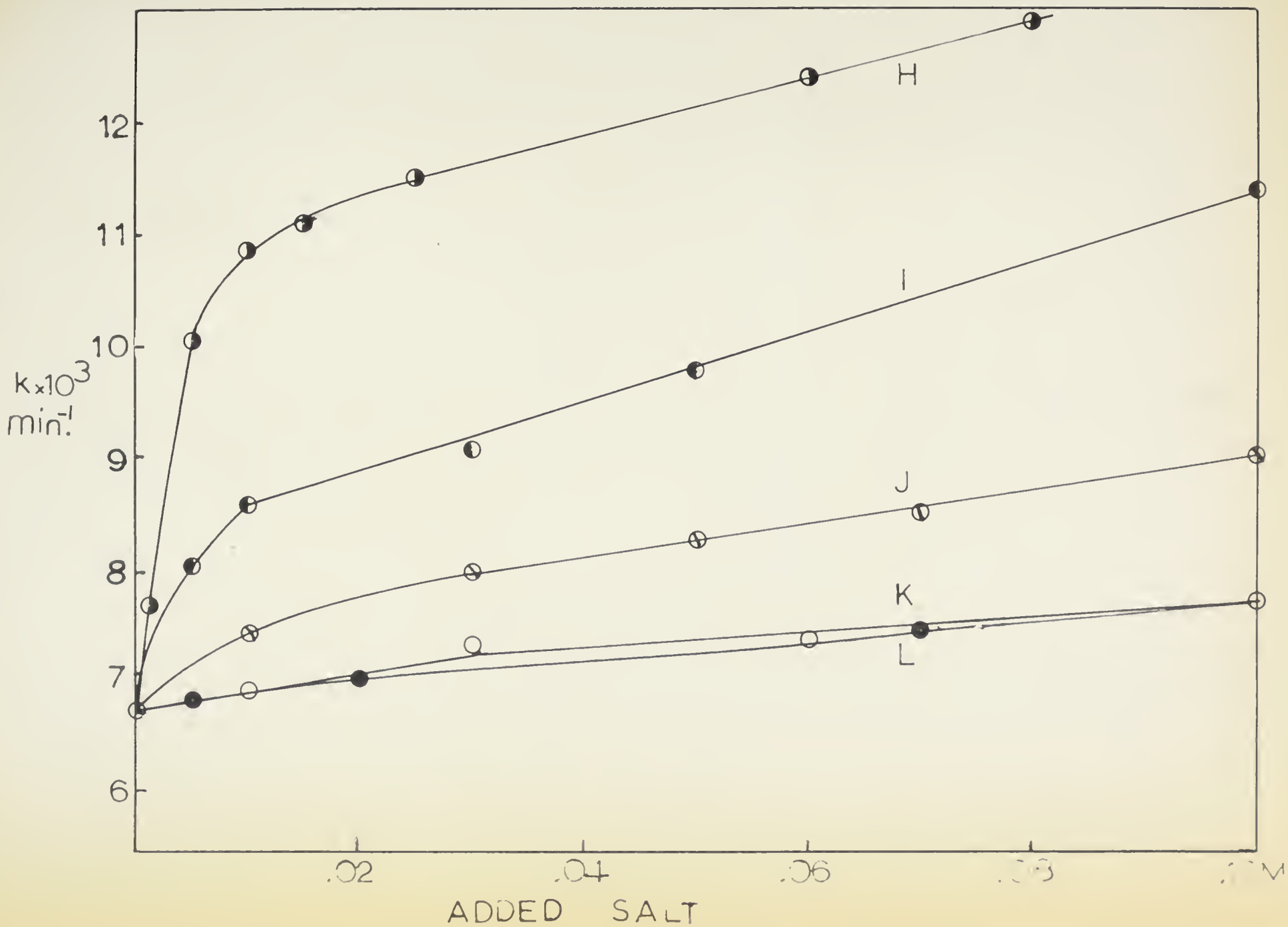

H
I
J
K
L
12
11
10
9
8
7
6
k x 10^3
min^-1
.02
.04
.06
ADDED SALT

Figure 20

PLOT OF LOGARITHM OF THE DIFFUSION CURRENT AGAINST TIME IN PRESENCE OF THREE DIFFERENT CITRATE CONCENTRATIONS AT 25°C.

A	0.2M Na citrate
B	.05M Na citrate
C	.005M Na citrate

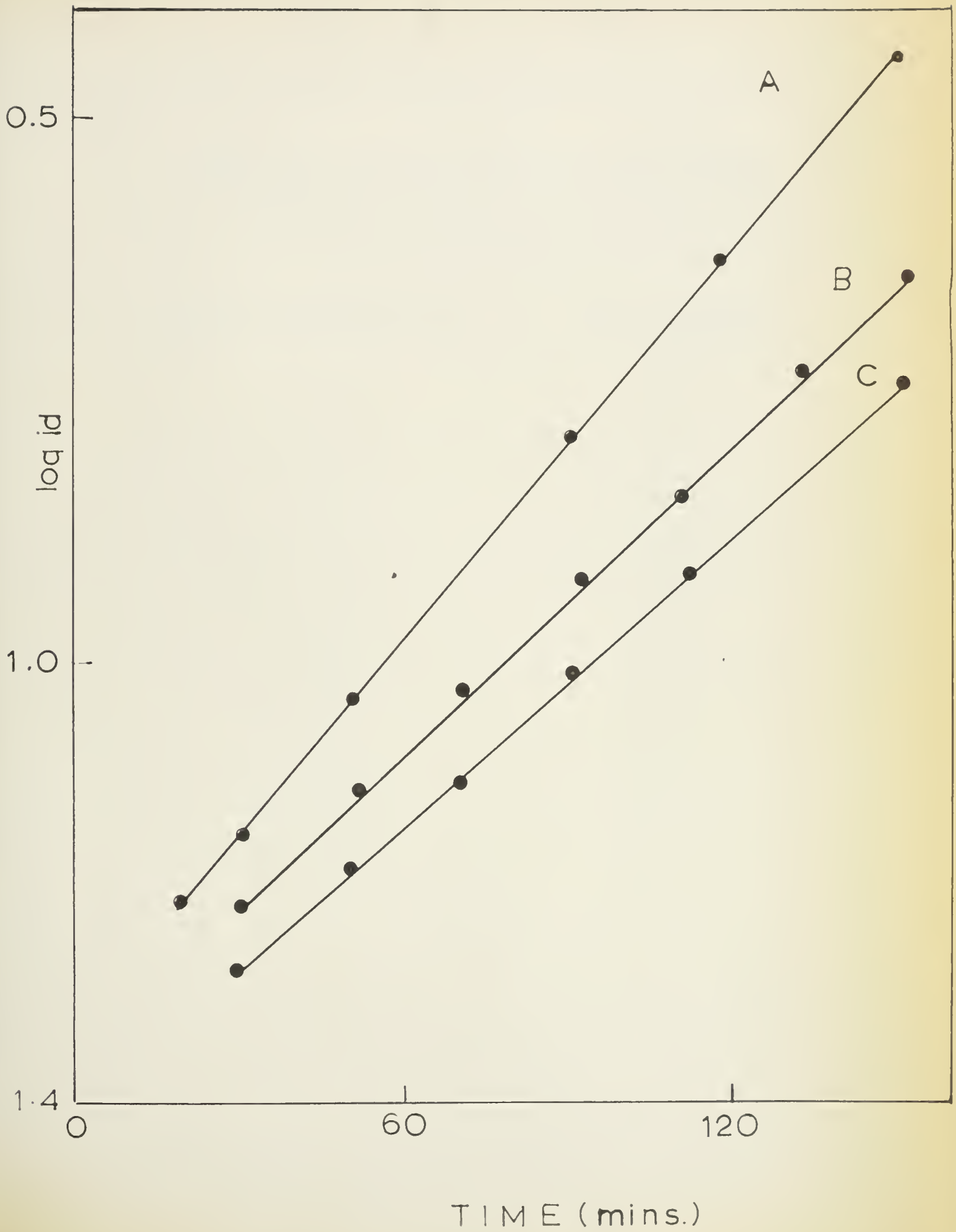

A
B
C
0.5
1.0
1.4
log id
0
60
120
TIME (mins.)

TABLE XXIII

EFFECT OF SODIUM CITRATE UPON THE RATE OF AQUATION OF $Cr(NH_3)_5Br^{++}$ AT 25°C.

Citrate concentration	$k \times 10^3$ min^{-1}
-	6.30
1×10^{-4}	6.41
5×10^{-4}	6.98
10^{-3}	7.49
2×10^{-3}	8.80
3×10^{-3}	9.65
5×10^{-3}	10.4
10^{-2}	10.9
2×10^{-2}	11.3
3×10^{-2}	11.5
5×10^{-2}	12.0
10^{-1}	13.2

TABLE XXIV

EFFECT OF SODIUM SULPHATE ON THE RATE OF AQUATION OF $Cr(NH_3)_5Br^{++}$ AT 25°C

Sulphate concentration	$k \times 10^3$ min^{-1}
-	6.30
4×10^{-4}	6.58
1×10^{-3}	7.13
3×10^{-3}	7.54
6×10^{-3}	8.17
1×10^{-2}	8.51
2.5×10^{-2}	9.21
8×10^{-2}	10.6
1.8×10^{-1}	10.8
3×10^{-1}	12.3
6×10^{-1}	13.9
1.0	14.9

TABLE XXV

EFFECT OF SODIUM p-PTHALATE ON RATE OF AQUATION OF $Cr(NH_3)_5Br^{++}$ AT 25°C

p-Pthalate Concentration	$k \times 10^3$ min^{-1}
-	6.30
10^{-2}	6.41
2×10^{-2}	6.55
7.0×10^{-2}	7.02

TABLE XXVI

EFFECT OF SODIUM MALEATE UPON RATE OF AQUATION OF $Cr(NH_3)_5Br^{++}$ AT 25°C

Maleate Concentration	$k \times 10^3$ min^{-1}
2×10^{-3}	6.30
5×10^{-3}	7.75
10^{-2}	9.55
1.5×10^{-2}	10.4
2.5×10^{-2}	11.0
6×10^{-2}	11.9
8×10^{-2}	12.4
10^{-1}	13.0

TABLE XXVII

EFFECT OF SODIUM o-PTHALATE ON RATE OF AQUATION OF $Cr(NH_3)_5Br^{++}$ AT 25°C.

o-Pthalate Concentration	$k \times 10^3$ min^{-1}
-	6.30
5×10^{-3}	7.55
10^{-2}	8.10
3×10^{-2}	8.55
5×10^{-2}	9.30
10^{-1}	10.9

TABLE XXVIII

EFFECT OF SODIUM MALONATE ON RATE OF AQUATION OF $Cr(NH_3)_5Br^{++}$ AT 25°C.

Malonate Concentration	$k \times 10^3$ min^{-1}
-	6.30
5×10^{-3}	7.06
1×10^{-2}	7.48
1.5×10^{-2}	7.85
2×10^{-2}	8.00
3×10^{-2}	8.45
5×10^{-2}	8.95
7×10^{-2}	9.20
1×10^{-1}	9.78

TABLE XXIX

EFFECT OF SODIUM FUMARATE ON RATE OF AQUATION OF $Cr(NH_3)_5Br^{++}$ AT 25°C.

Fumarate Concentration	$k \times 10^3$ min^{-1}
-	6.30
10^{-2}	6.90
3×10^{-2}	7.50
7×10^{-2}	8.00
1×10^{-1}	8.56

TABLE XXX

EFFECT OF SODIUM SUCCINATE ON RATE OF AQUATION OF $Cr(NH_3)_5Br^{++}$ AT 25°C

Succinate Concentration	$k \times 10^3$ min^{-1}
-	6.30
2.5×10^{-3}	6.55
7.5×10^{-3}	6.92
1.25×10^{-2}	7.20
2×10^{-2}	7.23
3×10^{-2}	7.4
5×10^{-2}	7.67
7×10^{-2}	8.05
1×10^{-1}	8.48

TABLE XXXI

EFFECT OF SODIUM OXALATE ON RATE OF AQUATION OF $Cr(NH_3)_5Br^{++}$ AT 25°C

Oxalate Concentration	$k \times 10^3$ min^{-1}
-	6.30
4×10^{-4}	6.33
1×10^{-3}	6.65
2×10^{-3}	6.78
5×10^{-3}	7.10
8×10^{-3}	7.45
1×10^{-2}	7.48
2×10^{-2}	7.70
4×10^{-2}	8.10
7×10^{-2}	8.62
1×10^{-1}	9.10

The effect of anions on the aquation rate of the chloro complex has also been investigated, but not in as much detail as for the bromo complex. The data in Table XXXII give values of the rate constant for the aquation of the chloro complex in the presence of different anions at 45°C. The ionic strength was kept constant at .02. The specific catalysing effects of the various anions on the chloro complex parallels their effect on the bromo complex. Fig. 21 shows a comparison of the catalysing effect of citrate on the bromo and chloro complexes. These data were obtained from Tables XXIII and XXXII respectively. The bromo complex was investigated at 25.0°C and the chloro at 45.0°C. From fig. 22, it would seem that citrate catalysis is the same for both chloro and bromo complex.

TABLE XXXII

EFFECT OF SODIUM CITRATE UPON THE RATE OF AQUATION OF $Cr(NH_3)_5Cl^{++}$ at 45°C.

Citrate Concentration	$k \times 10^3$ min^{-1}
7×10^{-4}	7.32
2×10^{-3}	8.25
5×10^{-3}	10.25
1.57×10^{-2}	10.36
1.0×10^{-1}	10.42
2×10^{-1}	13.8
5×10^{-1}	15.6

Figure 21

Comparison of the effect of citrate on the aquation rate of chloro and bromo complex.

A $Cr(NH_3)_5Br^{++}$ at 25°C

B $Cr(NH_3)_5Cl^{++}$ at 45°C

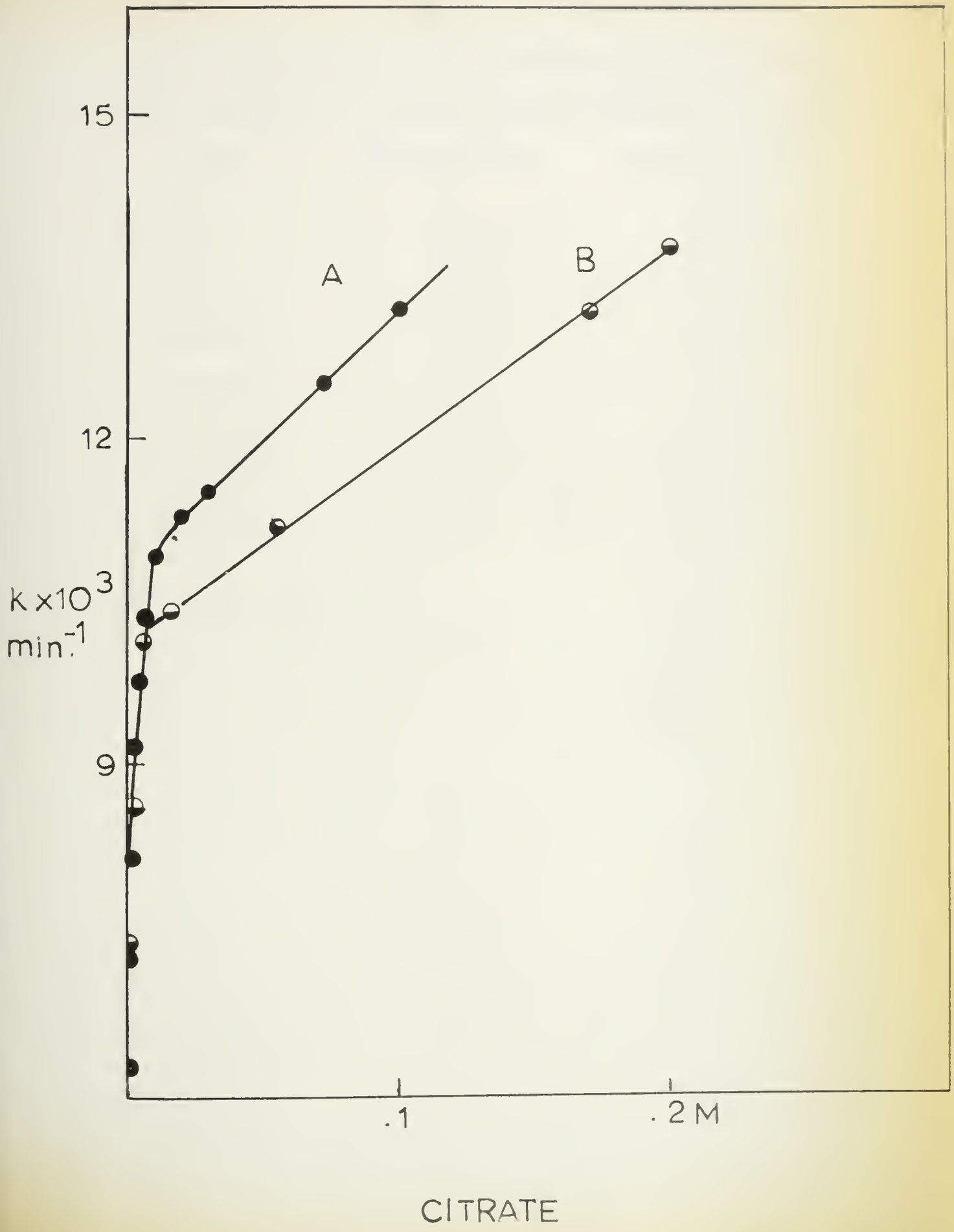

15
12
9
k x10^3
min.^-1
A
B
.1
.2 M
CITRATE

TABLE XXXIII

EFFECT OF DIFFERENT ANIONS ON THE RATE OF HYDROLYSIS OF $Cr(NH_3)_5Cl^{++}$ AT CONSTANT IONIC STRENGTH[a] $\mu = 0.2$

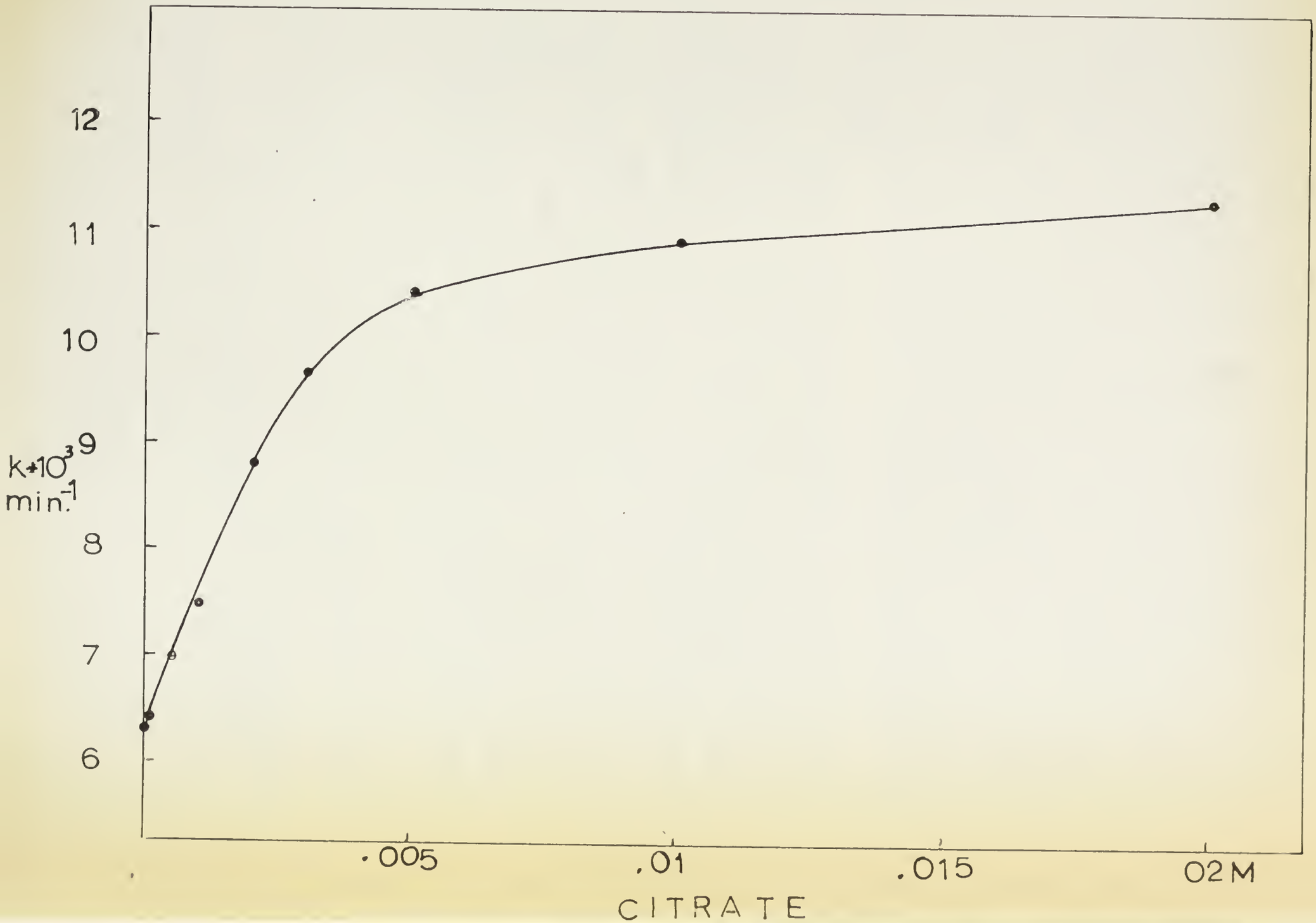
Salt	Concentration	$k \times 10^3$ min^{-1}
Cl^-	.2	6.04
SO_4^{--}	.0313	7.63
Oxalate	.0313	9.61
Malmonate	.0313	6.85
Succinate	.0313	7.95
Fumarate	.0313	7.02
Tartrate	.0313	7.82
Citrate	.0157	10.36

[a] Temperature 45°C

Figure 22

Effect of citrate on rate of aquation of

$Cr(NH_3)_5Br^{++}$ at 25°C


12
11
10
9
8
7
6
k*10^3
min.^-1
.005
.01
.015
.02 M
CITRATE

Figs. 18 and 19 show that the addition of small amounts of salt produced very marked acceleration of the rate of reaction. For the strongly catalysing ions citrate and maleate, the acceleration was linear in anion concentration until the salt was present at roughly equivalent concentration to the chromium present (10^{-3} molar). Further addition of salt increased the reaction rate still further but not so markedly. When salt concentration was greater than .02M, a linear relation between the reaction rate and added anion concentration was obtained.

Figure 22 shows the effect of citrate on the aquation rate of the bromo complex. This is the same curve as in fig. 18 but with the scale expanded to show the linearity of the curve at low citrate concentrations.

The anions studies seem to fall roughly into charge defined groups, according to their effects on the rate. The trivalent ion citrate, had a greater effect than the divalent anions which had a greater effect than the monovalent ions. The following parameters have been used to characterize the curves of figs. 18 and 19:

(a) The observed rate at .01M salt concentration divided by the rate in .01M perchloric acid, $\left(\frac{k_{.01}}{k_0}\right)$

(b) The slope (m) of the curve at high salt concentration.

The values of these parameters are shown in Table XXXIV.

The enhancement in the rate of aquation produced by the polyvalent anions is extremely sensitive to the total ionic strength of the solution. Table XXXV shows the effect of sodium perchlorate on citrate catalysis for the aquation of the chloro complex at 45°C.

TABLE XXXIV

EFFECT OF POLYVALENT ANIONS U ON THE RATE OF AQUATION OF $Cr(NH_3)_5Br^{++}$ AT 25°C

Salt	Rate at .01M $k_{.01}$	$\frac{k_{.01M}}{k_0}$	slope x 10^2 (liter, min^{-1}, $mole^{-1}$)
p-Pthalate	6.45	1.02	1.00
Fumarate	7.00	1.11	1.50
Succinate	7.10	1.13	1.42
Oxalate	7.45	1.18	1.75
Malonate	7.55	1.20	1.95
o-Pthalate	8.0	1.27	3.0
Sulphate	8.5	1.35	2.55
Maleate	10.3	1.63	2.7
Citrate	10.9	1.73	2.60

TABLE XXXV

EFFECT OF IONIC STRENGTH UPON CITRATE CATALYSIS OF THE AQUATION OF $Cr(NH_3)_5Cl^{++}$ AT 45°C

Citrate (Molar)	$NaClO_4$ (Molar)	$k \times 10^3$ min^{-1}
0.0	0.01	5.85
0.004	0.0	8.74
0.004	0.1	6.65
0.0	0.1	5.70
0.004	1.0	4.54
0.0	1.0	4.30

The temperature coefficient of the aquation of bromopentammine chromium (III) bromide in the presence of sulphate and citrate were investigated at four different concentrations of the anion.

TABLE XXXVI

RATE CONSTANTS FOR THE AQUATION OF $Cr(NH_3)_5Br^{++}$ IN PRESENCE OF VARYING CONCENTRATIONS OF CITRATE AT DIFFERENT TEMPERATURES

Citrate Concentration	.001	.003	.02	.05
Temperature °C				
0°	.268	.319	.401	.416
25°	7.50	9.65	11.10	12.0
45°	82.8	98.9	117.0	124.6

TABLE XXXVII

RATE CONSTANTS FOR THE AQUATION OF $Cr(NH_3)_5Br^{++}$ IN PRESENCE OF VARYING CONCENTRATIONS OF SULPHATE AT DIFFERENT TEMPERATURES

Sulphate Concentration	.001	.003	.02	.05
Temperature °C				
0	.235	.253	.314	.324
25	7.15	7.55	9.05	9.84
45	64.9	72.5	89.2	95.2

Figures 23 and 24 show the plots of the pseudo first order rate constant against $1/T$. The activation energies calculated from these plots are given in Table XXXVII.

In figs. 25 and 26 are plotted the rate constant (at .01M salt concentration) for the aquation of $Cr(NH_3)_5Br^{++}$ in various anions against the equilibrium constants for the association of both $Cr(NH_3)_5Cl^{++}$ and $Co(NH_3)_6^{+++}$ with the same anions.

These data were obtained from Table XLI.

Figure 23

Effect of temperature on the aquation rate in presence of varying concentrations of citrate.

A .001M Sodium citrate

B .003M Sodium citrate

C .02M Sodium citrate (curve displaced downwards by a factor of 10).

D .05M Sodium citrate (curve displaced downwards by a factor of 100).

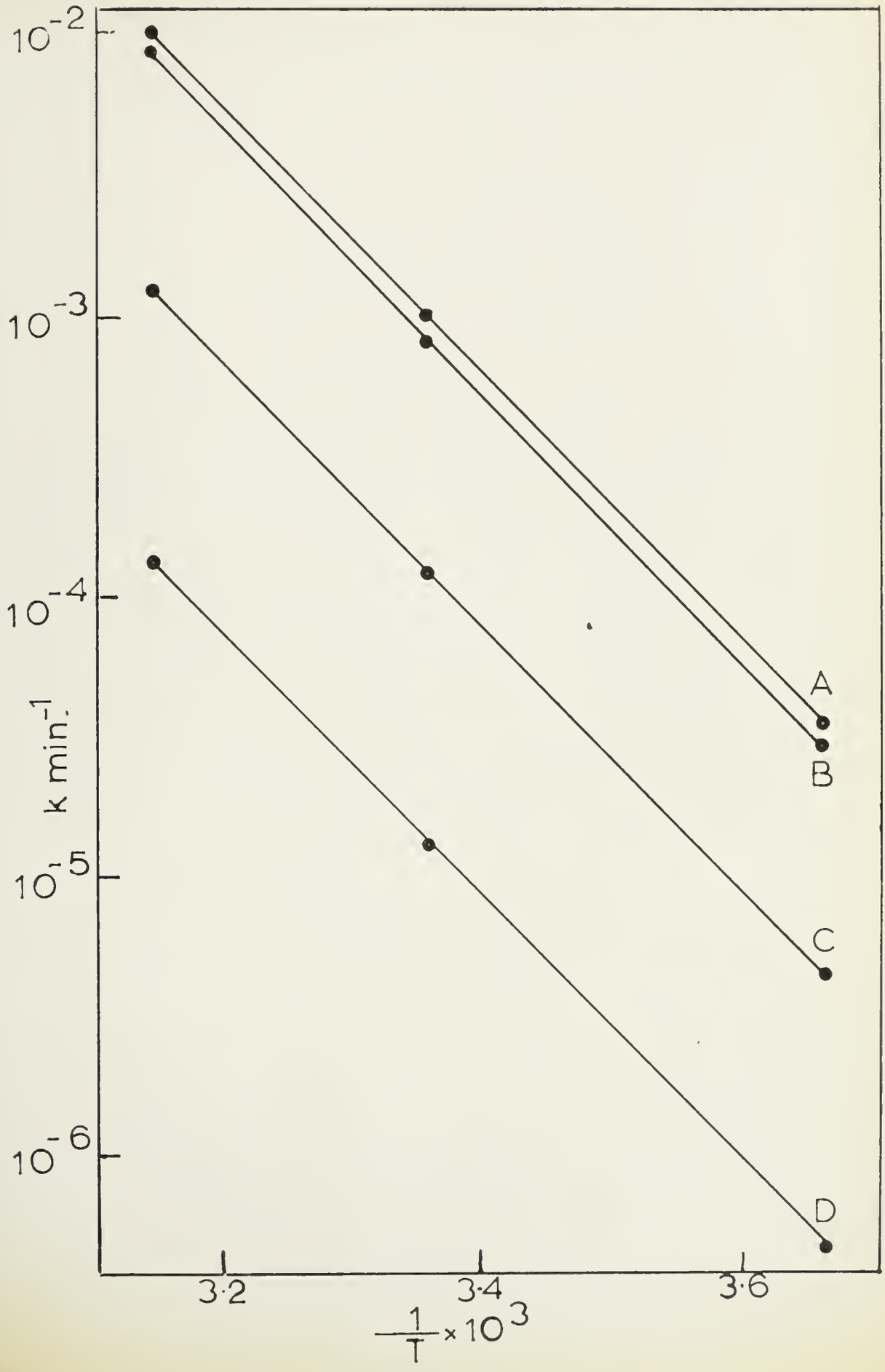

10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
k min^{-1}
A
B
C
D
3·2
3·4
3·6
$\frac{1}{T} \times 10^3$

Figure 24

EFFECT OF TEMPERATURE ON THE AQUATION RATE IN PRESENCE OF VARYING CONCENTRATIONS OF SULPHATE

E .001M Sodium sulphate

F .003M Sodium sulphate (displaced downwards by a factor of 10).

G .02M Sodium sulphate

H .05M Sodium sulphate (displaced downwards by a factor of 10).

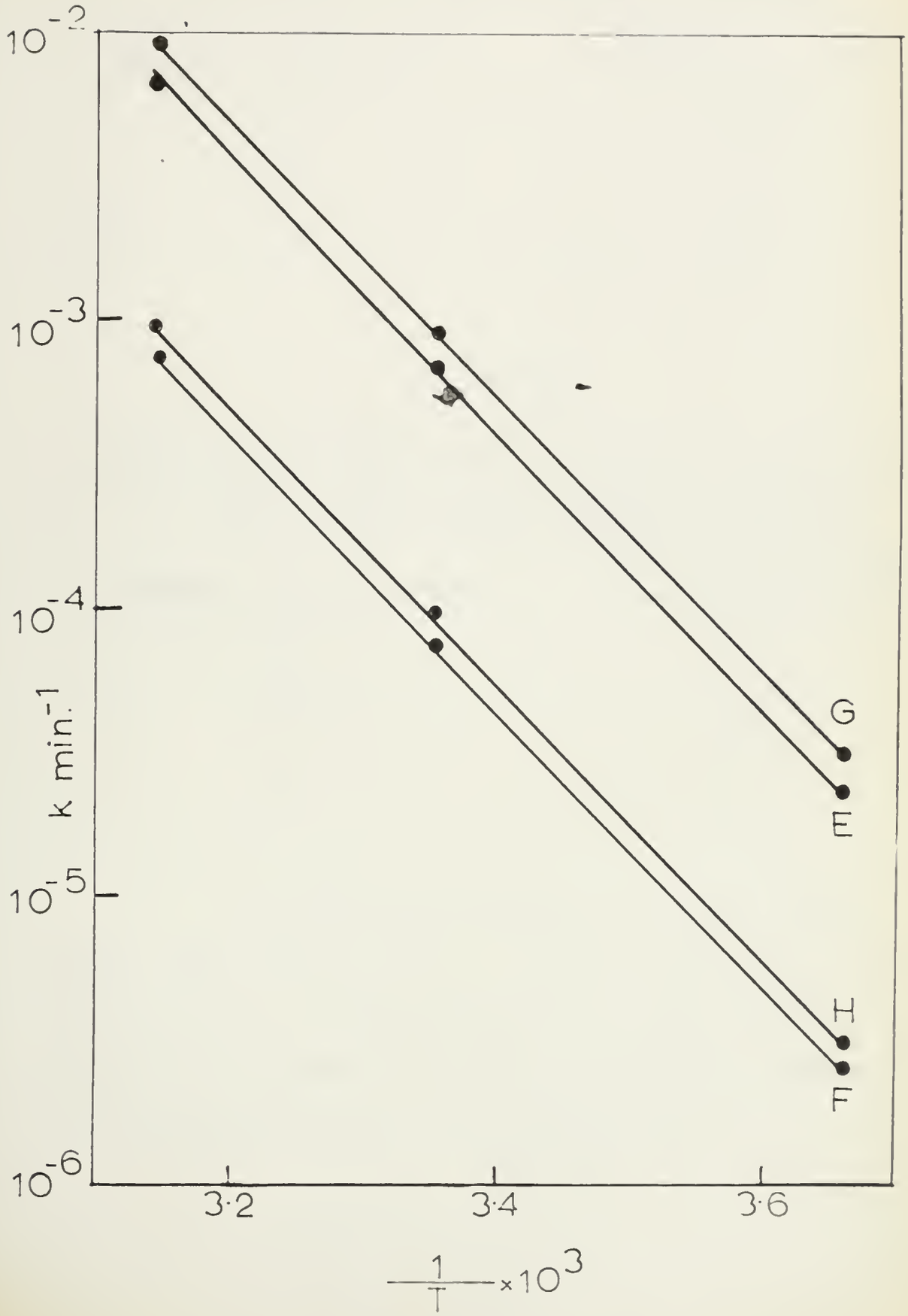

10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
k min^{-1}
G
E
H
F
3·2
3·4
3·6
$\frac{1}{T} \times 10^3$

TABLE XXXVIII

ACTIVATION ENERGIES FOR THE AQUATION REACTION OF $Cr(NH_3)_5Br^{++}$ IN THE PRESENCE OF CITRATE

Citrate Concentration	Activation Energies k cal ±.3
.001	22.1
.003	22.0
.02	21.9
.05	21.7

TABLE XXXIX

ACTIVATION ENERGIES FOR THE AQUATION OF REACTION OF $Cr(NH_3)_5Br^{++}$ IN THE PRESENCE OF SULPHATE

Sulphate Concentration	Activation Energies k cal. ± .3
.001	22.0
.003	21.9
.02	22.0
.05	21.9

The activation energy is almost constant within experimental error. In the presence of citrate, there does seem a slight decrease in the activation energy as the citrate concentration increases. This however, is small and may be insignificant.

Figure 25

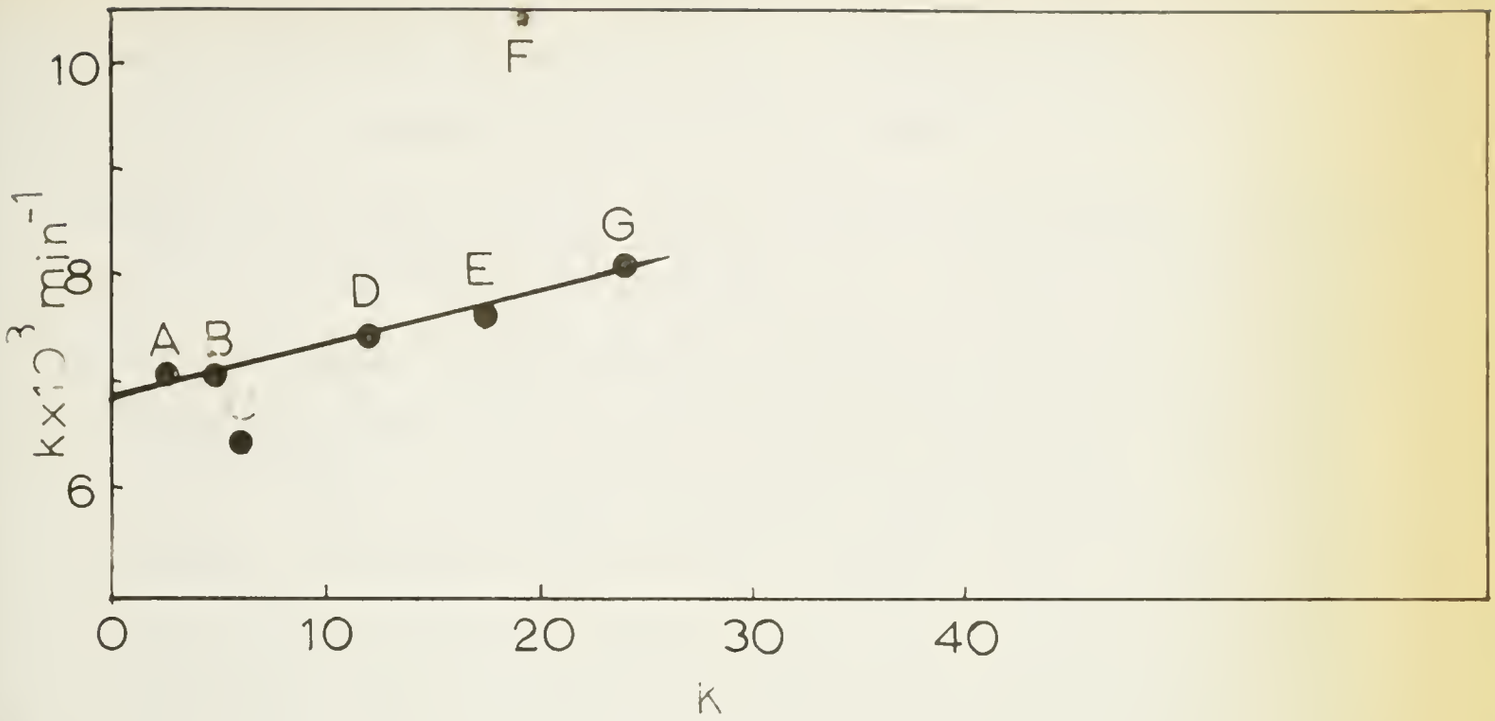
Plot of the observed rate constant for aquation of $Cr(NH_3)_5 Br^{++}$ (at .01M salt concentration) in presence of various anions, against the equilibrium constant for the association of $Cr(NH_3)_5 Cl^{++}$ with the same anions.

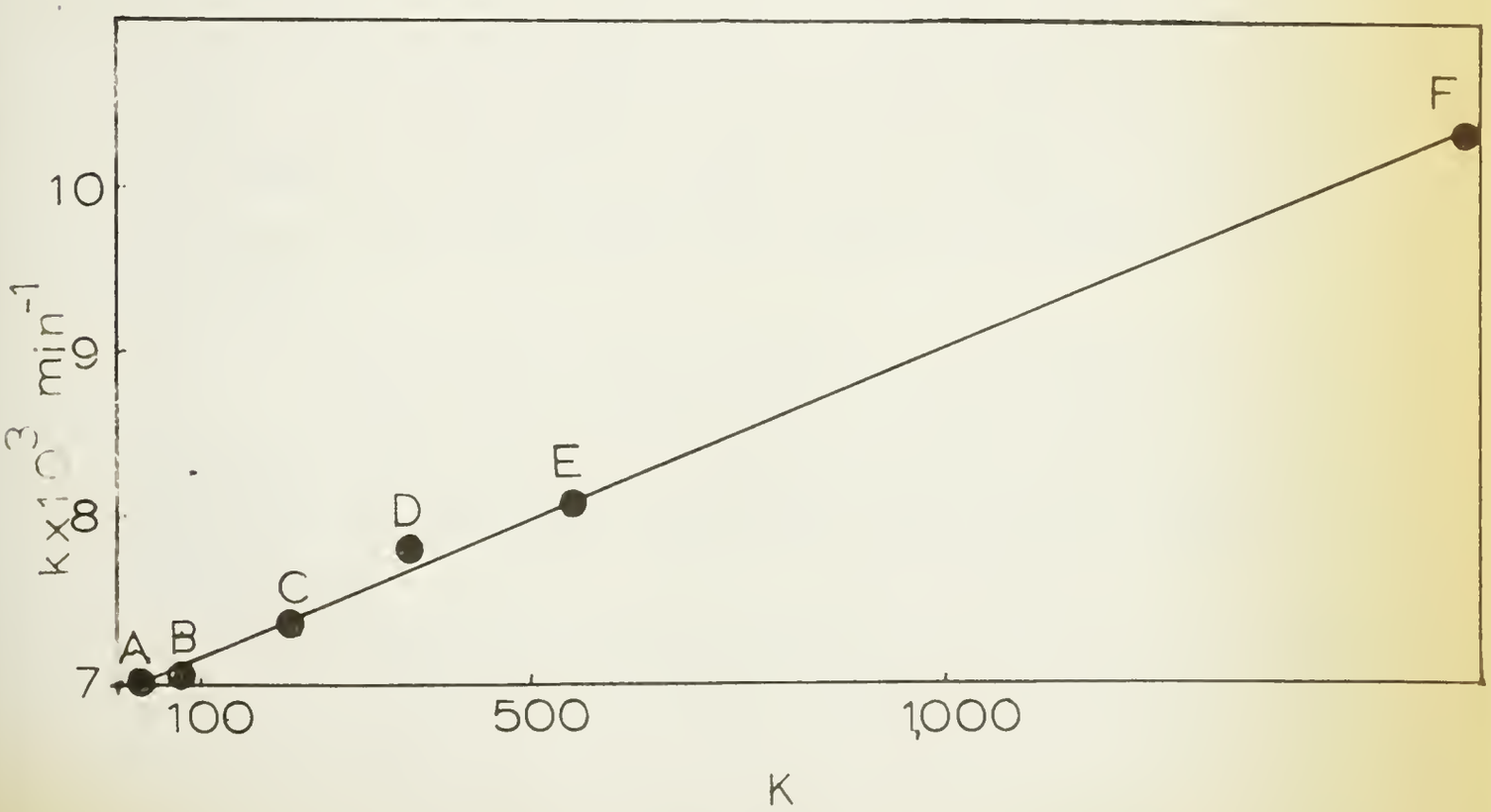
A. Fumarate
B. Succinate
C. p-Phthalate
D. Oxalate
E. Malonate
F. Maleate
G. o-Phthalate

Figure 26

Plot of the observed rate constant for the aquation of $Cr(NH_3)_5 Br^{++}$ (at .01M salt concentration) in presence of various anions, against the equilibrium constant for the association of $Co(NH_3)_6^{+++}$ with the same anions.
K for $Co(NH_3)_6^{+++}$ with various anions were obtained from ref. (87).

A. Fumarate
B. Succinate
C. Oxalate
D. Malonate
E. Maleate
F. o-Phthalate


10
8
6
$k \times 10^3$ min^{-1}
A
B
D
E
F
G
0
10
20
30
40
K


10
9
8
7
$k \times 10^3$ min^{-1}
A
B
C
D
E
F
100
500
1,000
K

Discussion

The effect of salts on the rate of aquation of halopentamminechromium (III) complexes do not seem explicable on the basis of the Bronsted-Debye relation (LXII).

$$\ln k = \ln k_o + 2Z_A Z_B \alpha\sqrt{\mu} \qquad \text{(LXII)}$$

where k_o is the reaction rate constant at infinite dilution, k is the observed reaction rate, Z_A and Z_B are the charge on the reactant ions A and B, respectively, α is a constant which depends on the solvent and μ is the ionic strength.

For the aquation reaction which involves reaction between a divalent cation (the complex) and a neutral molecule (water) the Bronsted relation would predict that the rate should be unaffected by added salt. The Bronsted equation is only valid when the ionic strength of the solution is less than .01M. Of the anions investigated, only perchlorate, chloride, bromide, iodide, and nitrate had little or no effect on the rate, up to a concentration of .01M. However, at higher ionic concentrations, the rate constant may change, because of changes in the activity coefficients of neutral molecules, which are affected by higher ionic strengths.

Huckel (67) has extended the above equation by including a term in the first power of the ionic strength to reproduce the activity coefficient of an ion at higher concentrations.

$$\ln k = \ln k_o + bu \qquad \text{(LXII)}$$

This predicts a linear relation between logarithm of the rate constant and the ionic strength. The data on the effect of salts again do not fit this relation as it is the rate, and not the logarithm of the rate, which appears to be linearly dependent on the ionic strength.

Bateman, Hughes and Ingold (68) introduced a theory for the interpretation of salt effects based on the requirements of the transition state in a reaction. Their theory is based on the fact that, if charge separation is involved in the transition state, then addition of neutral salts will help to separate the charges. This can be looked upon as a medium effect in which addition of salts increases the dielectric constant, and facilitates charge separation. This effect has been observed for a number of solvolytic reactions of organic compounds, such as alkyl halides (69). As expected, salt effects of this kind are more marked in solutions of lower dielectric constant than in water solution.

On the basis of Ingold's theory, a small positive salt effect would be expected in the aquation of halopentamminechromium (III) ions, since the reaction involves charge separation in the transition state by any mechanism. For all the anions investigated, with the exception of perchlorate, there is a possibility of specific interaction with the complex to account for the increased rate observed. The observed decrease in the rate of aquation in the presence of perchlorate ion is opposite to that predicted on the basis of Ingold's

theory. Since the chromium complex is originally divalent, and since the reaction is carried out in aqueous media, the small increase in dielectric constant, on addition of salt, would not be expected to produce very much increase in rate. This is proved from the small positive salt effects observed for the hydrolysis of alkyl halides in aqueous solution (70).

The decrease in rate on addition of 1.0 molar sodium perchlorate is less than 10%. This could be accounted for in terms of an activity effect, or competition for water, thus effectively reducing the activity of water.

The catalysing effect of the various anions investigated, cannot be accounted for in terms of a unified equation. Other workers (39), (40), (41) have observed this specificity of the rate on the nature of the anion, but, prior to this study, only a few anions, such as perchlorate nitrate, sulphate and azide, had been investigated. These salt effects have been attributed to specific ion pair formation, between the complex and the added anion.

For the strongly catalysing anions (as shown in figs. 18 and 19) the salt effect produced a two stage acceleration of rate. At low salt concentration an initial steep rise in rate was observed, followed by a subsequent smaller increase in rate at higher concentrations of added salt. The second salt effect is again both specific and linearly dependent on the salt concentration. This effect is characterised by a much lower slope than the initial effect.

Since previous studies on the effect of anions were limited to inorganic ions, this pattern of two distinct salt effects was not well defined, as can be seen in fig. 18 for the effect of sulphate on the reaction rate. There is, however, one example where the above type of distinction between the salt effects could be made; i.e. the hydrolysis of cis $Co\ en_2\ Cl_2^+$ in a solution of sodium azide in methanol (43). Since the dielectric constant of methanol is less than that of water, ion pair formation would be enhanced in the methanol solution.

Basolo and Pearson have interpreted the effect of azide on the rate of hydrolysis of $Co\ en_2\ Cl_2^+$ by superimposing the effects of ion pair formation between the reactants, and ionic strength effect on the magnitude of the ion pair formation constant.

The mechanism they propose is also valid for the effect of anions upon the aquation of halopentamminechromium (III) complexes.

In solution the free complex ion will be in equilibrium with the associated complex, as given by equation LXIV.

$$Cr(NH_3)_5Br^{++} + A^{n-} \underset{}{\overset{fast}{\rightleftharpoons}} Cr(NH_3)_5\ BrA^{2-n} \qquad \text{(LXIV)}$$

The association constant K will be given by equation LXV.

$$K = \frac{\left[Cr(NH_3)_5\ BrA^{\ 2-n}\right]}{\left[Cr(NH_3)_5\ Br\right]^{2+}\left[A\right]^{n-1}} \qquad \text{(LXV)}$$

The observed increase in rate is due to the faster aquation of the ion pair (equation LXVI).

$$Cr(NH_3)_5\ BrA^{n-2} + H_2O \xrightarrow{k_2} Cr(NH_3)_5\ H_2O^{n-3} + Sn^- \qquad \text{(LXVI)}$$

When ion pair formation is not complete, the normal aquation of $Cr(NH_3)_5\ Br^{++}$ complex, will also be taking place simultaneously.

$$Cr(NH_3)_5\ Br^{++} + H_2O \xrightarrow{k_1} Cr(NH_3)_5\ H_2O^{+++} + Br^- \qquad \text{(LXVII)}$$

The observed rate will be the sum of these two individual rates and is given by equation LXVIII.

$$\begin{aligned} \text{Rate} &= k_{obs}\left[Cr(NH_3)_5\ Br^{++} + Cr(NH_3)_5\ BrA^{n-}\right] \\ &= k_1 . Cr(NH_3)_5\ Br^{++} + k_2 . Cr(NH_3)_5\ BrA^{2-n} \end{aligned} \qquad \text{(LXVIII)}$$

Substituting for $Cr(NH_3)_5\ BrA^{2-n}$ from equation LXV

Then:

$$\begin{aligned} \text{Rate} &= k_{obs}\left[Cr(NH_3)_5\ Br^{++} + K \cdot Cr(NH_3)_5\ Br^{++} \cdot A^{n-}\right] \\ &= k_1 \cdot Cr(NH_3)_5\ Br^{++} + k_2 \cdot Cr(NH_3)_5\ Br^{++} \cdot K \cdot A^{n-} \end{aligned} \qquad \text{(LXIX)}$$

On rearranging:

$$\begin{aligned} k_{obs} \cdot Cr(NH_3)_5\ Br^{++}\left[1 + K\ A^{n-}\right] = \\ Cr(NH_3)_5\ Br^{++}\left[k_1 + k_2\ K . A^{n-}\right] \end{aligned} \qquad \text{(LXX)}$$

The observed rate constant is then equal to

$$\frac{k_1 + k_2 . K . A^{=}}{1 + K . A^{=}} \qquad \text{(LXXI)}$$

where k_1 is the rate constant for the reaction of free $Cr(NH_3)_5\ Br^{++}$, k_2 is the rate of dissociation of the associated $Cr(NH_3)_5\ Br \cdot A^{2-n}$ and K is the equilibrium constant for the formation of ion pairs.

The aquation reaction of the complex ion in the presence of salt does not appear to involve a bimolecular attack upon the halopentamminechromium (III) ions, since the reaction is first order, even in the presence of small concentrations of added salt. Furthermore, the sole primary product of the reaction is observed to be the hydroxypentamminechromium (III) ion. The resulting hydroxy complex reacts slowly with the added anion but at a rate which is much slower than the aquation rate.

The sensitivity of the salt effect to ionic strength of the solution, shown in table XXXV is a further indication that ion pairs are involved in the reaction rate. The addition of 1.0 molar sodium perchlorate in presence of .004M citrate reduced the rate almost to the value obtained at the same ionic strength in the absence of citrate. Taube and Posey (40) proposed the following equation to interpret the effect of ionic strength on the association constant of some cobalt complexes.

$$\log K_a = \log K_o - \frac{6.10\sqrt{\mu}}{1 + 1.50\sqrt{\mu}} \qquad \text{(LXXII)}$$

where K_a is the association constant at ionic strength μ, K_o is the association constant at zero ionic strength.

Equation LXXII predicts the variation of the association constant from zero ionic strength to nearly one. The numerical value of K_a changes by two orders of magnitude over this range. It is therefore, not surprising that sodium perchlorate has such a marked effect on citrate catalysis.

If the enhancement in aquation rate is due to ion pair formation between the complex and the added anion, then the observed rate should show a dependence on the magnitude of the association constant for the ion pair. In figs. 25 and 26 are plotted the experimentally observed values for the rate constant at .01 M added anion against the constants for association of the anions with both the chloropentamminechromium (III) complex and also cobalt (III) hexammine salt, respectively. In both cases, good agreement was obtained between the observed rate and the magnitude of the association constants. The association constants for the chloropentamminechromium (III) complexes were determined by a procedure to be described later and are reported in table XLI. The data for the association constants of various anions with hexammine cobalt (III) ion were obtained by Peacock and James (87). From the data in fig. 25, maleate appears to be out of line with the behavior of other anions. It has not been possible to explain this discrepancy, especially since the association constant of maleate with hexammine cobalt (III) ion appears to be normal. Repeated measurements of the association constant between the chlorocomplex and maleate ion gave reproducible values. It is not surprising that there is such a good correlation between the rate data for chromium and the association constants for heammine cobalt (III) ion since the change in the association constant for different anions will depend only on the anion, and will be the same whether the metal complex is cobalt or chromium, provided they are

both structurally similar (i.e. same size and environment).

The association constants for cobalt are, as would be expected, from the extra charge on the cobalt, higher than for the corresponding chromium complexes, and are probably more reliable than the chromium ones. This is due to the fact that the observed pH change on association is very much smaller for chlorpentamminechromium (III), than for hexamminecobalt (III), and is therefore more susceptible to errors.

It has been observed that the half wave potentials for the reduction of $Cr(NH_3)_5 X^{++}$ are shifted to more negative potentials in the presence of the various anions. The diffusion current is also lower. Many workers (71), (72) have attributed the shift in half wave potential, and decrease in the diffusion current, to ion pair formation between the complex and the anion. Since the polarographic waves of chromium (III) complexes are irreversible, it was not possible to calculate association constants for the ion pair from the shift in half wave potential. The data in table VI show the magnitude of the shifts in half wave potential obtained with perchlorate and sulphate anions.

It is conceivable that ion pair formation, between the halo complexes and the salt, could influence the rate of aquation in two ways: either by charge transfer from anion to the metal, or by stabilizing the transition state. If charge transfer occurred, then there would be an increase in electron density on the chromium atom, thus facilitating dissociation of the outgoing halide ligand.

Increasing the electron density on chromium would certainly inhibit attack by a nucleophilic reagent, such as a water molecule, in a displacement mechanism. If the catalysing effect of the anion is due to stabilization of the transition state, a bimolecular displacment of the halide by water would be retarded due to steric factors. If the mechanism involves attack by a water molecule, then, in the presence of citrate, the reaction should be retarded on steric grounds alone. This is contrary to what is observed since the rate is markedly increased. The acceleration of the rate of aquation by added anions does not seem explicable in terms of an SN_2 mechanism.

Winstein (72), (73) has observed somewhat similar salt effects when studying solvolysis reactions of certain arenesulfonates in acetone solutions. Added salts produced a two-stage acceleration of rate, as has been observed for the halopentamminechromium (III) complexes. At low salt concentrates, an initial steep rise in rate was observed, followed by a subsequent small increase in rate, almost perfectly linear in salt concentration. The initial steep rise in solvolysis rate on addition of salt, is referred to as a special salt effect, whilst the latter pattern is called the normal salt effect. Winstein attributes the special salt effect to the surpression of ion pair return in the system. shown below. Winstein (74) distinguished between three variaties of carbonium ion intermediates in acetolysis of various systems.

The solvolysis scheme proposed is shown in fig. 27.

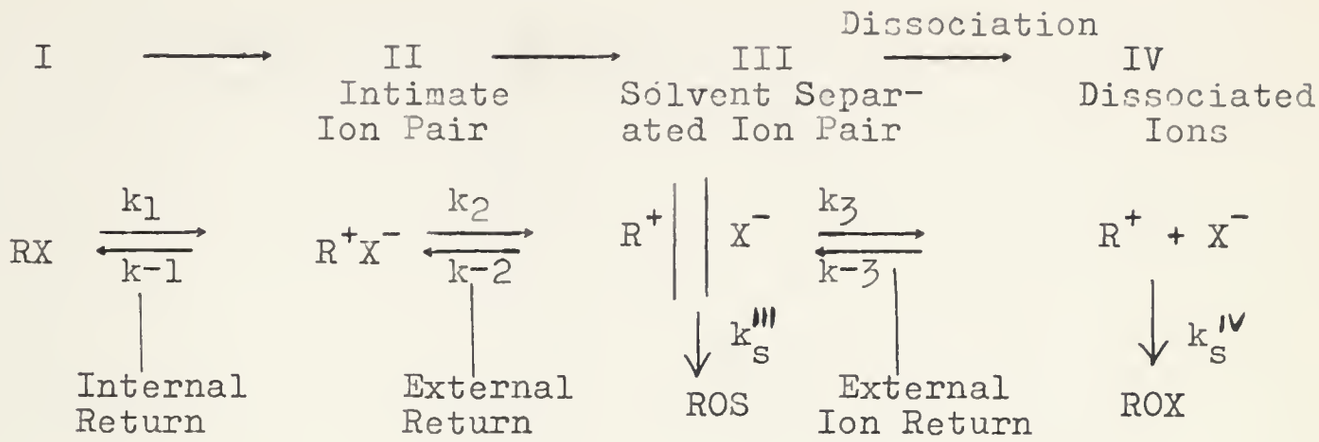


Figure 27. Scheme for Solvolysis of RX → ROS

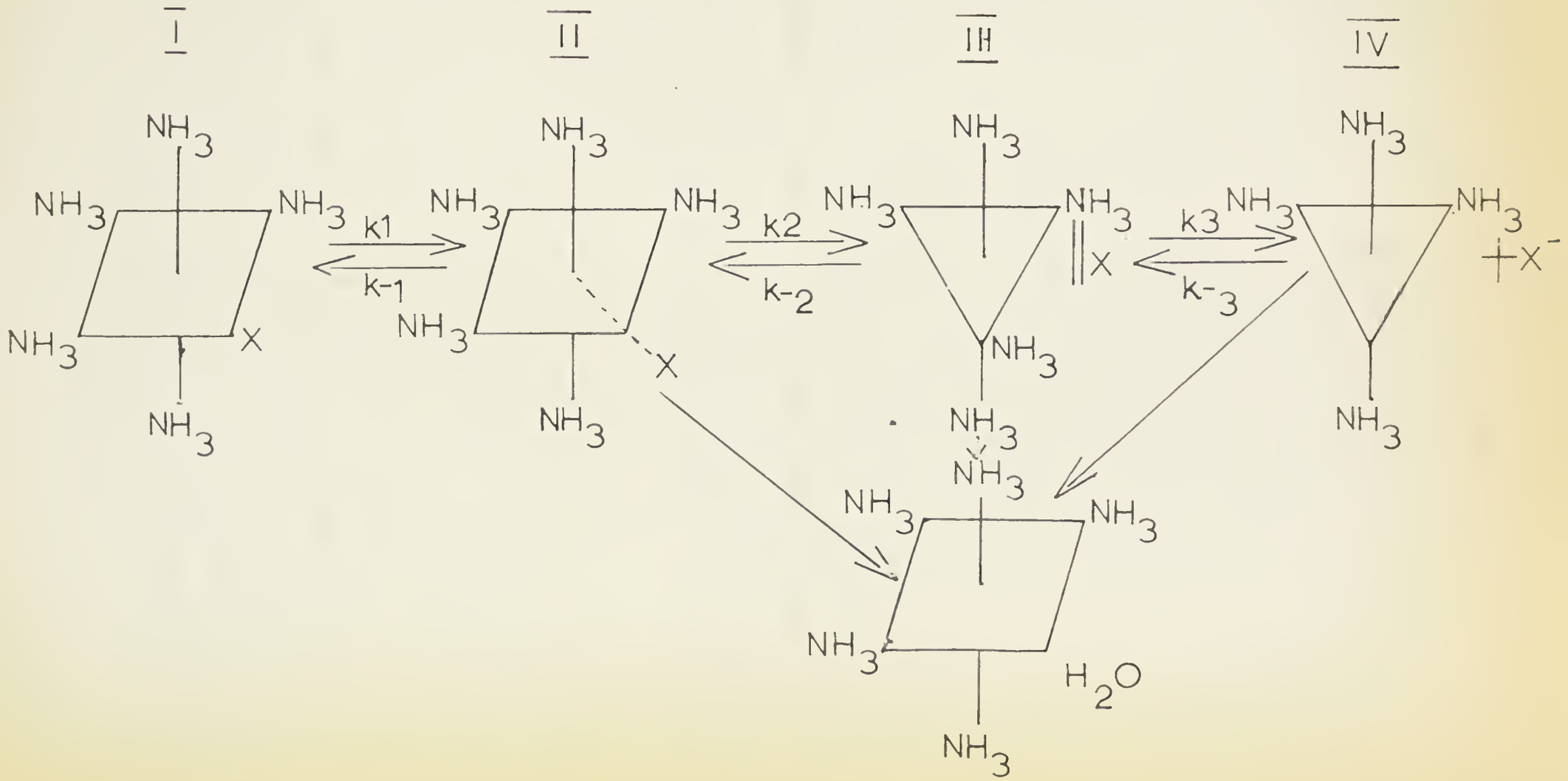
ROS is the solvolysis product of the reaction. The effect of the added salt is believed to involve diversion of a carbonium ion pair to a new ion pair species, thus surpressing ion pair return.

This scheme for the solvolysis of RX can be envisaged for the solvolysis of the halopentamminechromium (III) complexes. Fig. 28 shows the expected intermediates for the solvolysis of an octahedral complex by the above scheme.

The first step to give the intimate ion pair is envisaged as lengthening of the metal halogen bond with the complex still maintaining its original octahedral stereochemistry. The second step probably involves collapse of the original octahedral structure to give a five co-ordinated trigonal bi-pyramid configuration. This intermediate in Winstein's scheme is called a solvent separated ion pair. This then goes to give the dissociated ion. Any one of the above three intermediates could react with water to give the aquo product.

Figure 28

Scheme for aquation of an octahedral complex.


I
II
III
IV
NH3
X
k1
k-1
k2
k-2
k3
k-3
X-
H2O

If aquation proceeds via separated ions, then according to Batemen, Hughes and Ingold (75), it should be possible to detect the presence of such intermediate, by a mass law effect. Hydrolysis of the bromo and chloro complex in presence of bromide and chloride respectively, did not produce a mass law effect, as was shown in fig. 17. It appears that separated ions are not involved in the rate determining step by an SN_1 lim. mechanism. The two remaining possibilities are the intimate II pair and solvated ion pair III shown in fig. 28. Before deciding which intermediate is involved in the transition state, it is desirable to know more about the structure of the ion pair. From figs. 18 and 19 showing the effect of differenct salts on the rate of aquation of the bromo complex, it is possible to separate the anions roughly into three charge defined groups, such that the trivalent ions had a greater effect than the divalent ions which, in turn, had more effect than the monovalent ions.

According to Bjerrum's therory (76) of ion association, the extent of ion pair formation is primarily dependent on the charges of the ion involved (the higher the charge, the greater the degree of ion pair formation). It is, therefore, not surprising that the greatest effect on the rate is produced by citrate, and the least effect by the monovalen ions. There is, in contrast with the predictions of the simple theory, a considerable variation in the effects produced by divalent anions. This was shown in figs. 18 and 19. Of the divalent anions

produced the greatest effect, with the observed rate being only slightly lower than that found for citrate at an equivalent concentration. Fumarate, which is the corresponding trans isomer of maleate, had only a very slight accelerating effect on the rate. Similarly, o-pthalate produced a considerably greater effect than p-pthalate. It appears that steric factors must also play an important role in ion pair formation. The anion would be expected to attach itself on the side of the complex away from the leaving group. This would be expected both on steric and electrostatic grounds since the permanent dipole of the molecule will tend to repel a negatively charged ion on the same side as the leaving group. From studies on the aquation of cis and trans dichloro bis-(ethylenediamine) cobalt (III) complex (77) it was observed that basic anions accelerated the rate of aquation of the cis isomer but had little or no effect on the trans isomer. The cis complex has a permanent dipole which would favour association with basic anions on the side of the complex away from the two chloride groups. The importance of a permanent dipole is further borne out by the fact that maleate produces a much greater change in the reaction rate than fumarate, and similarly o-pthalate much faster than p-pthalate.

There appears to be at least two ways in which the anion could be associated with the complex, so as to produce the observed effects. It can do so either through hydrogen bonding between the carboxyl group of the anion and the nitrogen

of the ammine ligands, or by direct bonding to the chromium atom. If direct bonding occurs, then the anion would have to be situated on the face of the octahedron with bonding involving donation of electrons to the metal t_{2g} vacant orbitals. In order to achieve this kind of bonding, the metal orbitals would have to overlap with the anion ligand orbitals. It is not unreasonable to expect an overlapping of the orbitals, even though the basic anion is outside the first coordination sphere. The fact that charge transfer spectra are observed in the ultra violet for such complexes, is evidence for orbital overlap. Charge transfer absorption spectra have been observed for the hexammine and also aquopentamminecobalt (III) complexes (78),(79) with sufficiently polar ions, such as thiocyanate, iodide, bromide and chloride.

If the effect of basic anions on the rate were due to hydrogen bonding with the nitrogen, the ion pair formed would be as shown in fig. 29.

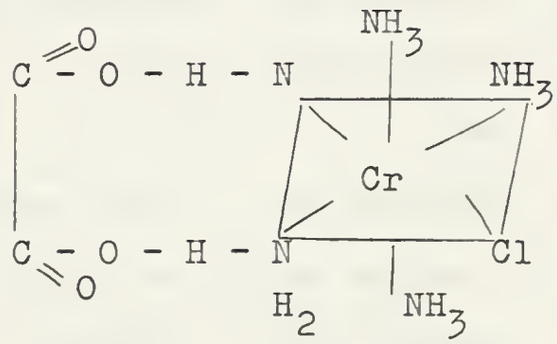


Figure 29. Hydrogen bonding between oxalate and $Cr(NH_3)_5\,Cl^{++}$ complex.

On the basis of hydrogen bonding, as shown above, it is difficult to see how effective charge transfer from

the carboxyl group to the metal atom can take place at all. This type of hydrogen bonding, if it occurs, would probably have some direct influence on the chromium to nitrogen bond. This should show up as a change in the visible absorption spectrum of the complex. The fact that there is no change in the visible absorption spectra in the presence of various anions would tend to argue against hydrogen bonding through the ammine nitrogens.

It appears that association probably takes place on the face of the octahedron, and not through hydrogen bonding. The anion with suitably situated π orbitals which can overlap with the t_{2g} orbitals of chromium will produce the largest effect on the rate.

With the available data, it is not possible to prove whether the greater effect produced by maleate and o-pthalate, in comparison to fumarate and p-pthalate, is due to stronger bonding or to a higher concentration of the associated complex present. The strong interaction of both maleate and o-pthalate can be accounted for in terms of greater induced electrostatic effect due to the presence of the double bond.

Since the added anions do not affect the visible absorption spectra of the complex, the anion cannot, therefore, be penetrating into the complex, or even interferring with the amine ligands. It could be argued that if orbital overlap takes place between a metal d orbital and ligand orbitals, then this interaction might be expected to interfere with the energy levels of the d orbitals and cause a change in

the visible absorption spectra. Since no change in the visible absorption spectra is observed even when a charge transfer spectrum is present, this would suggest that the association has no effect on the splitting of the energy levels. An alternative argument is that it is the metal 4d orbitals which are used in bonding. It is not possible to prove whether it is the 3d or 4d orbitals which are involved in bonding.

Ingold (16) postulated 4d type of bonding for aquation reactions by an SN_2 mechanism, in which bonding took place between the incoming water molecule and the metal 4d orbitals. This type of bonding would not be expected to interfere with the d absorption spectrum of the complex. For the dicarboxylic acid series $(CH_2)_n(COOH)_2$ the order of increasing rate and increasing stability constant was malonate > oxalate > succinate. The tendency for dicarboxylate stability to decrease as n increases is usually attributed to the less favourable entropy change that occurs when the chain between the two carboxyl groups is lengthened. If this were the only factor to be considered then oxalate should be more stable than malonate. It appears that other factors have to be taken into account. James, Monk and Davies (80), have suggested that the stability constant is dependent mainly on two factors, the hydration energy, and the energy of interaction of the associating ions. Since the cation is the same in all cases, i.e. the chloro complex, the only factor which has to be considered is the interaction energy

of association of the anion. The interaction energy of the associating ions is made up of at least two factors; the entropy effect and the solvation energy of the anion. The higher association constant and the correspondingly greater increase in rate of malonate over oxalate may be due to the fact that the oxalate ion, due to its smaller size, will have a higher solvation energy than the maleate ion.

In fig. 28, a proposed scheme for the possible intermediates involved in the aquation reaction of $Cr(NH_3)_5X^{++}$ by an SN_1 mechanism was given. The possibility of an SN_2 displacement mechanism seems unlikely on the basis of the observed specificity of the salt effects.

Since the aquation reaction is not affected by added common ion, the possibility of an SN_1 mechanism involving separated ions (i.e. IV fig. 28) can be ruled out. The two remaining possible intermediates are the intimate ion pair (II fig. 28) in which the complex still maintains its original octahedral stereochemical form, and the solvent separated ion pair (III fig. 28) in which the original octahedral structure collapses to a trigonal bi-pyramid.

If the aquation reaction involves a solvent separated ion pair, the resulting 5 co-ordinate intermediate would be expected to be very reactive, and to react with whatever happens to be near. It would then be expected that some of the anion present in solution would find its way into the product. This is not observed, since the aquo complex is always the first product of the aquation reaction. It is known, however,

that at much longer times, the anions, especially the di and trivalent organic anions, do enter into the first co-ordination sphere but at a much slower rate (27). The reaction of the aquo complex with citrate will be discussed later. Since the anion is not found in the reaction product, it would seem that the aquation reaction does not involve a solvent separated ion pair as the intermediate.

The intimate ion pair (II fig. 28), as an intermediate in the aquation reaction is, however, compatible with the observations made. Presumably, the first step in this mechanism is a stretching of the chromium to halogen bond with the complex still in a roughly octahedral configuration. During this process the water molecules around the halide ion become oriented in such a way that, as the halide ion leaves, a water molecule slips into position to complete the reaction.

Since the activation energy of the aquation reaction is virtually independent of both the nature and concentration of the added anion (tables XXXVIII and XL and figs. 23 and 24,) it would seem that the mechanism of the reaction is not changed by the presence of added ions. Added anions, by specific interaction with the complex, increase the electron density on chromium, thus facilitating the removal of a negative ligand.

In table XXXVIII, the activation energies in the presence of citrate do show a very slight decrease as the anion concentration increases. This difference, however, is almost within the experimental error. If this trend of decrease in the activation energy is real, than it is as would be predicted by the proposed mechanism.

If the effect of anions is to increase the electron density on chromium, then it would be expected that the activation energy for the dissociation of the chromium to halogen bond would decrease. Since the rate is only increased by a factor of two or three, at the most, in the presence of citrate and sulphate, the change in activation energy by this process would be expected to be small.

The catalysing effect exerted by various anions in the concentration range 0 to 5×10^{-3}M seems explainable in terms of specific association of the anion with the complex to give an ion pair.

In the salt concentration range .01 to .10 molar, the rate is again linearly dependent on the anion concentration, but the slope of the curve is very much smaller. The slope of this part of the curve also appears to be specifically dependent on the nature of the anion, since the greater the catalysing effect of the anion, as given by the parameter $\frac{k_{.01}}{k_0}$ in table XXIV, the greater is the slope (m) of the salt effect at high concentrations of anion. This could be explained by assuming that after one mole of anion is associated with complex to give an ion pair, then this ion pair is associated with another molecule of anion which causes a further increase in the rate. The observed increase in rate would not be expected to be as large, as the association constant for a second mole of anion with the complex must be small. Although the shapes of the curves can be accounted

for by this interpretation, it does not seem likely that the ion pair formed between the complex and anion, which will be negatively charged, will associate with another molecule of anion.

Another interpretation, which is probably more likely, is that the second part of the curve on salt effects at high concentration represents the effect of ionic strength on the ion pair. At higher salt concentration greater than .005M, the salt will exert two opposing effects. It will increase the concentration of ion pair due to mass action effect, thus resulting in acceleration of the observed rate. The second effect will be the effect of ionic strength on the formation of ion pair. This will reduce the effective concentration of ion pair in solution and result in a deceleration of the rate. From the shape of the curves in figs. 18 and 19 it appears that the first effect wins over the ionic strength effect, thus leading to an increased rate, but very much slower. The effect of ionic strength on the rate has been previously discussed. The data in table XXXV show that the ionic strength has a marked effect upon the reaction rate as a result of the decrease in effective concentration of ion pair present.

That the second salt effect at higher salt concentrations is due to the effect of ionic strength on the rate, and not further association of the complex can be seen if the curve for the effect of sodium maleate on the rate is examined fig. 19. The curvature which begins at approximately .003M in

maleate is due either to ionic strength decreasing the concentration of the associated complex present, or saturation with all the complex being in the associated form.

For the complex to be 90% in the associated form at a concentration of .003 molar in maleate, the magnitude of association constant would have to be about 3,000 (as calculated from equation LXXX). This is far too high; especially since the association constant between hexamminecobalt (III) ion and maleate is only about 1,600, and the chromium complex with one less positive charge would be expected to be much lower than this.

Since the other anions with the exception of citrate have much lower association constants than maleate, it can be presumed that the effect of salt on the rate at high concentrations of salt is an ionic strength effect on the magnitude of the association constants. This is confirmed by the data in table XXXV showing that increasing the ionic strength of the solution, whilst citrate concentration is kept constant, results in a marked decrease in the rate, which can be attributed to a decrease in the association constant.

V STUDIES ON THE ASSOCIATION BETWEEN HALOPENTAMMINE-CHROMIUM (III) COMPLEXES AND VARIOUS ANIONS

Since it is believed that the specific effects of added salts on the rate of aquation reactions of chromium (III) complexes are due to association of the complex to give an ion pair, it was decided that this could best be proved by an independent method for demonstrating the existence of such ion pairs.

The most general method for proving the existence and also for determining the equilibrium constant of outer sphere complexes, or ion pairs, has been made by observing the changes in the near-ultraviolet region of the spectrum. When various anions are added to a solution of complex salt, the absorption bands in the visible region of the spectrum are unaffected. However, the charge transfer absorption region is often markedly changed. This change, essentially consists of a shift of the intense band to longer wavelengths, and is due to outer sphere complexes or ion pairs. The shift to longer wavelengths has been attributed to charge transfer from the ligand to the metal atom (78).

From the spectral shifts in the presence of added anions, the equilibrium constants of association for many trivalent complexes have been determined (78).

Attempts were made to observe shifts in the near ultraviolet region for halopentamminechromium (III) complexes in the presence of various anions, such as citrate, maleate,

oxalate, sulphate, chloride, bromide, iodide and thiocyanate. The ultraviolet absorption spectra of the chromium (III) complexes were unchanged except in the presence of thiocyanate ion. Phillips and Plane (82) have also observed a shift in the ultraviolet absorption spectra for chloropentammine-chromium (III) complexes with thiocyanate.

In fig. 30 is shown a plot of the optical density for $Cr(NH_3)_5 Cl^{++}$ against thiocyanate concentration, at different wavelengths. The data for fig. 30 were obtained from table XL. It is apparent that the optical density increases linearly as the thiocyanate concentration increases. Even at 1.0M in thiocyanate the optical density still increased linearly. This would suggest that the association constant for $Cr(NH_3)_5 Cl^{++}$ with thiocyanate is very small, and that at 1.0M thiocyanate concentration ion pair formation is still not complete. As the association constant for $Cr(NH_3)_5 Cl^{++}$ with thiocyanate is so small, it was not possible to determine its value spectrophotometrically.

It is not completely understood why a charge transfer spectra was not observed for the other anions investigated. There appears to be two factors that affect the charge transfer spectra; one is the nature of the ion pair, and the other is the concentration of ion pair present.

On the basis of the association constants for $Co(NH_3)_6^{+++}$ with various anions (78) it would be expected that the association constant would be much greater for the di and tri-valent anions investigated, than for the thiocyanate

TABLE XL

EFFECT OF DIFFERENT THIOCYANATE CONCENTRATION ON THE CHARGE TRANSFER ABSORPTION SPECTRA OF $[Cr(NH_3)_5Cl]^{++}(ClO_4)_2$[a]

KSCN	$D_{275\ m\mu}$	$D_{280\ m\mu}$	$D_{290\ m\mu}$
.01	.035	.025	.012
.05	.077	.048	.025
.20	.215	.118	.070
.58	.465	.265	.110
1.0	.750	.455	.216

a) Chromium concentration .015M

ion. It appears that the nature of the associated anion plays an important role in determining whether an ion pair gives rise to an observed shift in the charge transfer spectra. The observed shift is no indication of the magnitude of the association constant as has been demonstrated for the association of $Co(NH_3)_6^{+++}$ with the halides (78). Iodide produces the greatest shift in the charge transfer absorption spectra but has the lowest association constant. This is probably due to the fact that the iodide ion is more polarisable than either bromide or chloride, thus facilitating transfer of electrons from ligand to metal. The thiocyanate ion, due to its large internal dipole, would be expected to favour donation of the electrons on the nitrogen to the metal atom, thus giving rise

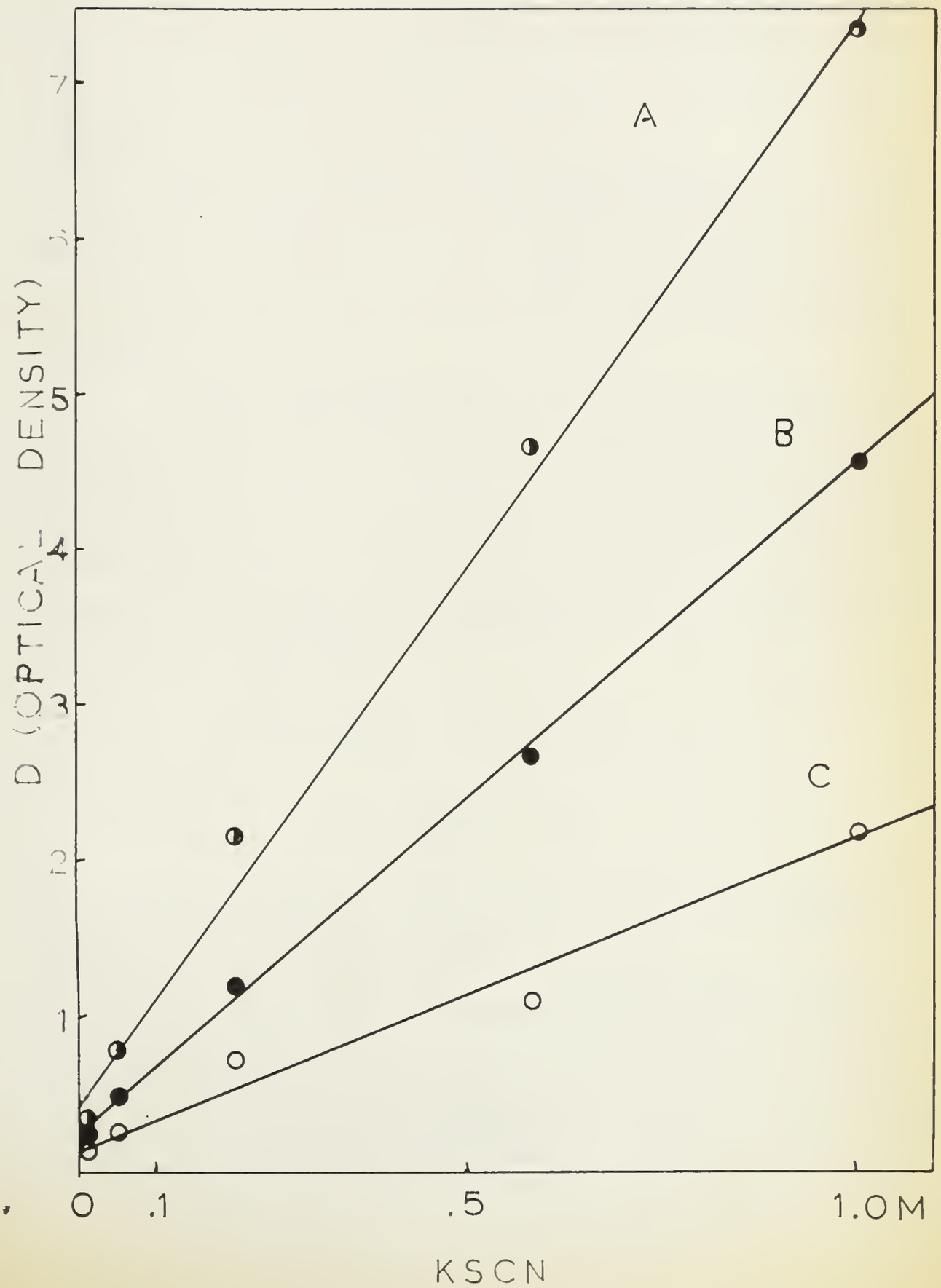
Figure 30

Plot of optical density for $Cr(NH_3)_5 Cl^{++}$ against concentration of added KSCN

A. Optical density at 275 mμ

B. Optical density at 280 mμ

C. Optical density at 290 mμ


D (OPTICAL DENSITY)
7
5
4
3
1
A
B
C
0
.1
.5
1.0M
KSCN

to a charge transfer spectra. This appears not to be the case for the anions of the various carboxylic acids, which do not give rise to a charge transfer spectra. There is, also, the possibility that charge transfer does take place even for the anions of the carboxylic acids, but at much lower wavelenghts where it is masked by the ultra violet absorption spectra of the anion.

Since it was not possible to determine the extent of association between the chromium (III) complexes and the various anions by spectrophotometry, another method was attempted.

When complex formation takes place between a metal cation and the anions of various carboxylic acids, a decrease in pH is observed. If a metal salt M is added to a solution of weak acid (HA) in equilibrium with its anion (A^-), then, the equilibria existing in solution will be given by equations LXXIII AND LXXIV.

$$HA \rightleftharpoons H^+ + A^- \qquad \text{(LXXIII)}$$

$$A^- + M^+ \rightleftharpoons MA \qquad \text{(LXXVI)}$$

The addition of metal salt M will result in an increase in the hydrogen ion concentration.

The association constant for the ion pair MA is given by equation LXXV.

$$K_a = \frac{[MA]}{[A^-][M^+]} \qquad \text{(LXXV)}$$

It should then be possible to determine the association constant between a metal complex, and the anions of various carboxylic acids. This method has been widely used under the name of "Bjerrum titration method", for determining the formation constants of a number of metal ions with the various anions of carboxylic acids (83). Since the formation constants of these complexes are usually large, the change in pH due to complex formation is usually substantial, thus making it possible to determine fairly accurately the value of the formation constants. This, however, is not the case for association between a metal complex and various anions as this would be expected to be a very weak interaction, consequently, with a much smaller change in pH.

A number of workers (84), (85), have reported a decrease in pH on the addition of a complex metal salt to a solution of different carboxylic acids. The decrease in pH paralleled the co-ordinating ability of the carboxylic acid, but there is no evidence that the anion penetrates into the first co-ordination sphere. It is generally accepted that the change in pH is due to outer sphere association of the complex with a particular anion. Cannan and Kibrick (86), have used this method for determining the equilibrium constants for the association of metals with the anions of various carboxylic acids. Peacock and James (87) have used the same technique for determining equilibrium constants between hexamminecobalt (III) ion and a number of anions of dicarboxylic acids. Their values are given in table XLII.

Since both the association constant and pH are very sensitive to ionic strength, this has either to be kept constant at a known value, or the ionic strength of the solution has to be evaluated. Peacock and James (87), by a series of successive approximations, calculated the ionic strength of the solution, and then corrected the pH data for the ionic strength.

Cannan and Kibrick (86) added a ten-fold excess of metal ion and assumed the ionic strength to remain constant at that of the added metal ion regardless of the extent of association. This, they show, is a justified approximation for the two extreme cases; i.e. 0% and 100% complex formation. For the two extreme cases the ionic strength varied by only 10%.

In this work the same technique as used by Cannan and Kibrick has been employed. The concentration of dicarboxylic acid in this investigation was .005M and that of the chromium complex .0333M. The total ionic strength of the solution was assumed to be constant at 0.1.

Experimental

A solution .005M in sodium or potassium hydrogen salt of the dicarboxylic acid was prepared by neutralising a weighed amount of the dicarboxylic acid with one half equivalent of sodium hydroxide, and diluting to volume in a volumetric flask. Ten ml. of this solution was pipetted into a 20 ml. beaker and the pH noted both before and after

the addition of sufficient potassium chloride so as to make the final solution 0.1M in potassium chloride. The pH measurements were made with a Beckman model 96 Zeromatic pH meter. To another 10 ml. aliquot, 0.1237 gms of chloropentamminechromium (III) perchlorate was added and the pH measured. All the pH measurements were made at 25°. The solutions were brought to this temperature in a 25° temperature bath.

From the difference in pH between the solution containing potassium chloride and the one with added chloropentamminechromium (III) perchlorate values for the association constants were evaluated. The association constants were calculated from a much simplified version of the method used by Cannan and Kibrick. So as to prove that the method used was a valid one, the experimental data of Cannan and Kibrick were taken and the association constants calculated.

The association constant for zinc and glycolic acid as given by Cannan and Kibrick, and as determined by the calculation described below are 83 and 88 respectively. It can therefore be assumed that the method described below is a valid one.

The purpose of adding potassium chloride to one of the samples was to apply a correction for the change in pH, due only to the increase in ionic strength of the solution upon addition of the chloro complex. It is assumed that the decrease in pH on addition of potassium chloride is due only to increase in the ionic strength of the solution.

The change in pH produced by the addition of complex, over and above that expected on the basis of the increase in ionic strength alone, was attributed to the formation of ion pair between complex and the dibasic anion, according to equations (LXXIII) and (LXXIV). Ion pair formation with the monovalent anion is assumed to be negligible. This assumption is shown to be reasonable on the basis of the association constants reported for metal ions with mono carboxylic acids (87).

Another assumption is, that only a one to one complex is formed. This again appears to be a valid assumption, since the resulting complex first formed would have no charge, and this uncharged unit would not be expected to pick up another mole of anion. The association constant between the chloropentamminechromium (III) complex and a variety of anions was calculated from the observed change in pH as follows:

The equilibria involved in a solution of the complex with sodium hydrogen carboxylate can be represented as follows:

$$H_2A \underset{}{\overset{K_1}{\rightleftharpoons}} HA^- + H^+ \qquad \text{(LXXV)}$$

$$HA^- \overset{K_2}{\rightleftharpoons} H^+ + A^= \qquad \text{(LXXVI)}$$

$$Cr(NH_3)_5Cl^{++} + A^= \overset{K_a}{\rightleftharpoons} Cr(NH_3)_5\,ClA \qquad \text{(LXXVII)}$$

The following relations can be written:

$$K_1 = \frac{[HA^-][H^+]}{[H_2A]} \qquad \text{(LXXVIII)}$$

$$K_2 = \frac{[A^=]\,[H^+]}{[HA]} \qquad \text{(LXXIX)}$$

$$K_a = \frac{[Cr(NH_3)_5\ ClA]}{[Cr(NH_3)_5\ Cl^{++}][A^{=}]} \qquad \text{(LXXX)}$$

K_a is the assocation constant for the complex and anion. Since concentration of H_2A under the experimental conditions used is small, its concentration can be neglected, thus only reactions (LXXVI) and (LXXVII) need to be considered. The difference in pH between the solution containing potassium chloride and that containing the chloro complex is assumed to be due to association of the chloro complex with the salt of the dicarboxylic acid. The conditions pertaining after the addition of potassium chloride will be referred to as initial conditions (i) whilst the final conditions after the addition of the chloro complex will be denoted by (f).

Initially $HA_i^- + A_i^= = .005$ (LXXXI)

finally $HA_f^- + A_f^= + Cr(NH_3)_5ClA = .005$ (LXXXII)

The change in pH as a result of association of complex with the anion represents the amount of HA^- which has dissociated after addition of the complex. Therefore, the final concentration of HA_f^- is given by equation (LXXXIII).

$$HA_f^- = HA_i^- - \Delta H^+ \qquad \text{(LXXXIII)}$$

By substituting into equation (LXXIX) the values for HA_f^-, H^+, and K_2, $A_f^=$ can be obtained. The concentration of the ion pair is given by equation (LXXXIV).

Then

$$\left[Cr(NH_3)_5\ ClA\right] = .005 - HA_f^- + A_f^= \qquad \text{(LXXXIX)}$$

and

$$K_a = \frac{\left[.005 - HA_f^- - A_f^=\right]}{\left[A_f^=\right]\left[0333 - (.005 - HA_f^- - A_f^=)\right]} \qquad \text{(LXXXV)}$$

Thus, K_a can be calculated.

Since the chloro complex itself was moderately acidic a correction had to be applied to the final pH of the solution after addition of the complex. This correction was calculated from the titration curve obtained by a pH titration of 10 ml. of .015 M chloro complex, with 0.0541 M sodium hydroxide. The titration curve is shown in fig. 31. The manner in which the correction was applied can best be illustrated by taking a specific example, eg. o-phthalate data from table (XLI.) From fig. 31, it requires .016 ml, of .0541 M NaOH to change the pH from 4.5 to 5.13, i.e. the pH after addition of the chloro complex. This amount of sodium hydroxide represents contribution of the complex to the observed pH change and can be looked upon as the amount of hydrogen ions released into the solution by the complex itself. This would react with $A^=$ to give HA^- so that the final concentration of HA^- will be greater by this amount.

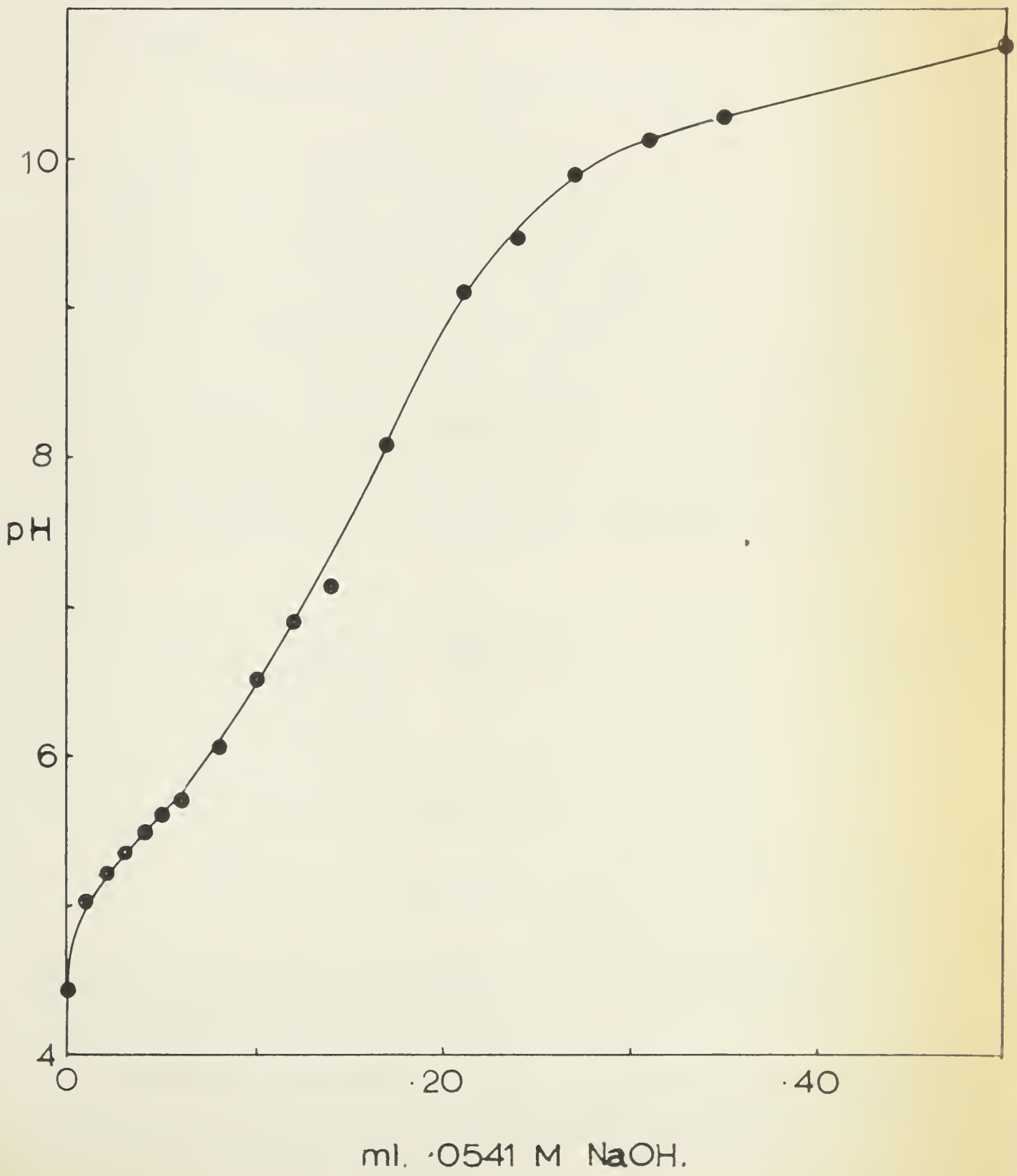
The concentration of HA_i^- is given by equation (LXXXVI)

$$HA_i^- = \frac{\left[A_i^=\right]\left[H^+\right]}{K_2} = \frac{\left[A_i^=\right] \times 3.89 \times 10^{-6}}{3.98 \times 10^{-6}} \qquad \text{(LXXXVI)}$$

$$\therefore\ HA_i^- = \frac{\left[A_i^=\right]}{1.023} \qquad \text{(LXXXVII)}$$

Figure 31

pH titration curve of $[Cr(NH_3)_5 Cl](ClO_4)_2$ with sodium hydroxide solution at 25°.


10
8
pH
6
4
0
·20
·40
ml. ·0541 M NaOH.

Originally, since only HA^- and $A^=$ are present

$$HA_i^- + A_i^= = .005 \qquad \text{(LXXXVIII)}$$

From equation (LXXXVII) and (LXXXVIII), HA_i^- and $A_i^=$ can be calculated;

$$A_i^= = .002528$$

$$HA_i^- = .002472$$

HA_i^- represents conditions when no association takes place. From titration curge fig. 31, 0.016 mls of .0541 M NaOH were required to bring 10 mls of .005 molar solution of the chloro complex to a pH of 5.13. This corresponds to .000868 moles of base. Therefore, the change in pH is equivalent to liberating .000868 m.moles of acid into the solution. This amount of acid neutralises a corresponding equivalent of $A^=$ to give HA^-.

Total

$$HA_f^- = .002472M + .0000868M \qquad \text{(LXXXIX)}$$

$$= .002558M.$$

This represents final concentration of HA^-.

Increase in HA^- due to change in pH:

$$(H^+_{final} - H^+_{original}) = (7.41 \times 10^{-6} - 3.89 \times 10^{-6})$$

$$= 3.52 \times 10^{-6} \qquad \text{(XC)}$$

This is so small in comparison to the total HA^- present that it can be neglected.

By substituting in values for K_2, HA_f^- and H_f^+ into equation (LXXVI) the concentration of A_f^- can be calculated.

$$A_f^- = .001374.$$

The concentration of the associated complex is then given by equation (XCI)

$$Cr(NH_3)_5\ ClA = .005 - (.001374 + .002588) \qquad (XCI)$$

$$= .001607$$

The concentration of the complex which is not associated is then:

$$Cr(NH_3)_5\ Cl^{++} = .0333 - .001067$$

$$= .0322$$

K, the association constant, is then given by

$$K = \frac{[Cr(NH_3)_5\ ClA]}{[Cr(NH_3)_5\ Cl]^{++}\ [A^{=}]} \qquad (XCII)$$

$$= \frac{[.001607]}{[.0322]\ [.001374]}$$

$$= 24.1$$

The values for the association constants of various anions with $Cr(NH_3)_5\ Cl^{++}$ calculated as shown above are reported in table (XLI)

TABLE XLI

ASSOCIATION CONSTANTS (K) FOR $Cr(NH_3)_5 Cl^{++}$ WITH VARIOUS ANIONS AT 0.1 IONIC STRENGTH AND 25°C.

Anion	Original pH	pH after addition of K Cl	pH after addition of $Cr(NH_3)_5Cl$	$A^{=}x10^3$	$HA^{-}x10^3$	Association Constant K
p-pthalate	5.30	5.09	4.98	2.711	1.75	6.1
Succinate	5.99	5.74	5.60	2.165	2.599	2.89
Oxalate	4.63	4.39	4.25	2.03	2.20	12.1
Fumarate	4.88	4.64	4.59	2.78	1.76	4.99
Maleate	6.60	6.38	5.99	1.53	2.60	17.6
Maleate	4.84	4.60	4.39	0.07	4.88	18.6
o-pthalate	5.69	5.41	5.11	1.37	2.56	24.1
Malonate	6.22	5.98	5.62	1.99	1.89	17.5
Malonate	6.24	6.03	5.78	1.21	0.92	18.6

Concentration of NaHA = .005M

Concentration of $\left[Cr(NH_3)_5 Cl\right] (ClO_4)_2$ = .0333M

In table (XLII) are tabulated the association constants of the various anions with both hexamminecobalt (III) ion and chloropentamminechromium (III) ion. In column 4 the rate of the aquation reaction of $Cr(NH_3)_5 Br^{++}$ at 25°C in presence of .01M anion is given.

TABLE XLII

COMPARISON OF (K_a) ASSOCIATION CONSTANTS, BETWEEN VARIOUS ANIONS AND BOTH $Co(NH_3)_6^{+++}$ AND $Cr(NH_3)_5Cl^{++}$

Anion	K_a (a) $Co(NH_3)_6^{+++}$	K_a (b) $Cr(NH_3)_5Cl^{++}$	k .01M x $10^3 min^{-1}$ for $Cr(NH_3)_5Br^{++}$
o-phthalate	556	24.1	8.0
Maleate	1,640	18.6	10.3
Malonate	345	18.0	7.55
Oxalate	204	12.1	7.45
Succinate	87	2.9	7.10
Fumarate	23	5.0	7.00
p-phthalate	---	6.1	6.45

a) K_a at ionic strength .01

b) K_a at ionic strength .1

Discussion

The values for the association constants between the various anions and $Co(NH_3)_6^{+++}$ are very much higher than the corresponding values for $Cr(NH_3)_5Cl^{++}$. This is mainly due to the difference in the charge on the complexes, as well as to a difference in the ionic strength. The association constants for the $Co(NH_3)_6^{+++}$ were determined at .01 ionic strength whilst those of chromium complexes were measured at 0.1. It would have been more desirable to obtain the association constants for the chromium complex at a lower ionic strength, but

this was not possible as the pH change would also be smaller, and thus more susceptible to errors.

Since the chlorpentamminechromium (III) perchlorate is more soluble than the bromopentamminechromium (II) bromide, and also since the rate of hyrdolysis is slower, this complex was used for all the pH measurements.

VI. BASE HYDROLYSIS REACTION

Experimental Results

Above pH 11.5, the hydrolysis reaction for the halopentamminechromium (III) complexes (figs. 13 and 14) obeys second order kinetics, with linear dependence on both the concentration of the complex and hydroxide ion. This reaction has been previously referred to as the base hydrolysis

$$Cr(NH_3)_5X^{++} + OH^- \rightarrow Cr(NH_3)_5OH^{++} + Cl^- \quad \text{(XCIII)}$$

where X is bromide, chloride or iodide.

The rate of the reaction is given by equation (XCIV).

$$\text{Rate} = k_b \left[Cr(NH_3)_5X^{++}\right] \left[OH^-\right] \quad \text{(XCIV)}$$

The hydrolysis of halopentamminechromium (III) complexes follow a similar pattern to that of the cobalt complexes, i.e. pH independent and pH dependent regions. The significant differences between the two complexes are, that for the cobalt complexes, the pH dependent region contributes at a much lower pH than it does for the chromium complexes, and that is is much faster than the aquation reaction. It has been observed (22) that the hydrolysis of the cobalt complexes are pH dependent even at a pH of 3. This observation has been interpreted to involve an SN_1CB mechanism for the base-hydrolysis of the cobalt (III) complexes.

The data of table (XLIII) show that the rate of the base hydrolysis reaction increases as the leaving

group varies from chloride to bromide to iodide in the same way as for the aquation reaction.

TABLE XLIII

RATE CONSTANTS FOR BASE HYDROLYSIS OF HALOPENTAMMINECHROMIUM (III) AND COBALT (III) COMPLEXES AT HIGH pH IN 0.1M PERCHLORATE SOLUTIONS

Reactant	$Cr(NH_3)_5Cl^{2+}$	$Cr(NH_3)_5Br^{2+}$	$Cr(NH_3)_5I^{2+}$
k_b(l. mole^{-1} min^{-1})	.11[a]	4.3[b]	220[a]
Reactant	$Co(NH_3)_5Cl^{++}$	$Co(NH_3)_5Br^{++}$	$Co(NH_3)_5I^{++}$
k_b(l. mole^{-1} min^{-1})	52[c]	3.6×10^2 [c]	-

[a] 25.0°

[b] 25.3° data from Dr. W. E. Harris

[c] data from reference 18.

For comparison purposes, rate constants for the base hydrolysis of the analogous cobalt complexes are also given in Table (XLIII.)

TABLE XLIV

RATIO OF THE RATES IODIDE TO BROMIDE, AND BROMIDE TO CHLORIDE FOR CHROMIUM (III) AND COBALT (III) COMPLEX AT BOTH HIGH AND LOW pH AT 25.0°C

Reactant	$Cr(NH_3)_5X^{2+}$	$Co(NH_3)_5^{2+}$
$\frac{k_1I^-}{k_1Br^-}$ (pH 1-10)	11.7	1.3
$\frac{k_bI^-}{k_bBr^-}$ (pH 11.5+)	51	-
$\frac{k_1Br^-}{k_1Cl^-}$ (pH 1-10)	11.0	3.8
$\frac{k_bBr^-}{k_bCl}$ (pH 11.5+)	40	70

k_1 refers to aquation rate

k_b to base hydrolysis rate

The data of table LXIV show that the ratio of rates, iodide to bromide, and bromide to chloride for both cobalt and chromium (III) complexes, are much greater for the base hydrolysis reaction than for the aquation reaction. This would indicate, on the surface at least, that the base hydrolysis reaction is more dependent on the nature of the metal to halogen bond, than is the corresponding aquation reaction. This might indicate that bond breaking is important to the

rate determining step. The rate constants for the base hydrolysis reaction of chloro and iodo complex were measured as a function of temperature. The data are given in table XLV.

TABLE XLV

RATE CONSTANTS FOR BASE HYDROLYSIS OF CHLORO AND IODO PENTAMMINECHROMIUM (III) IONS AT DIFFERENT TEMPERATURES

Reactant		$Cr(NH_3)_5Cl^{++}$ (a)	k_b min^{-1}	$Cr(NH_3)_5I^{++}$ (b)
Temperature	$1/T \times 10^3$			
0°	3.66	1.44×10^{-4}		---
1°	3.65	---		4.83×10^{-2}
10°	3.53	---		2.19×10^{-1}
25°	3.36	---		2.25
25.3^o	3.36	1.13×10^{-2}		---
45.0^o	3.15	1.48×10^{-1}		

(a) pH 13 in 0.1M NaOH

(b) pH 12 in .01M NaOH

Fig. 32 give plots of the pseudo first order rate constant against the reciprocal of the temperature for the base hydrolysis of halopentamminechromium (III) ions. Activation energies, frequency factors and entropies of activation calculated from the slopes of the lines, are given in table (XLVI).

Figure 32

Effect of temperature on the base hydrolysis reaction chloro and iodopentamminechromium (III) ions.

A. $Cr(NH_3)_5 Cl^{++}$ at pH 13.0

B. $Cr(NH_3)_5 I^{++}$ at pH 12.0

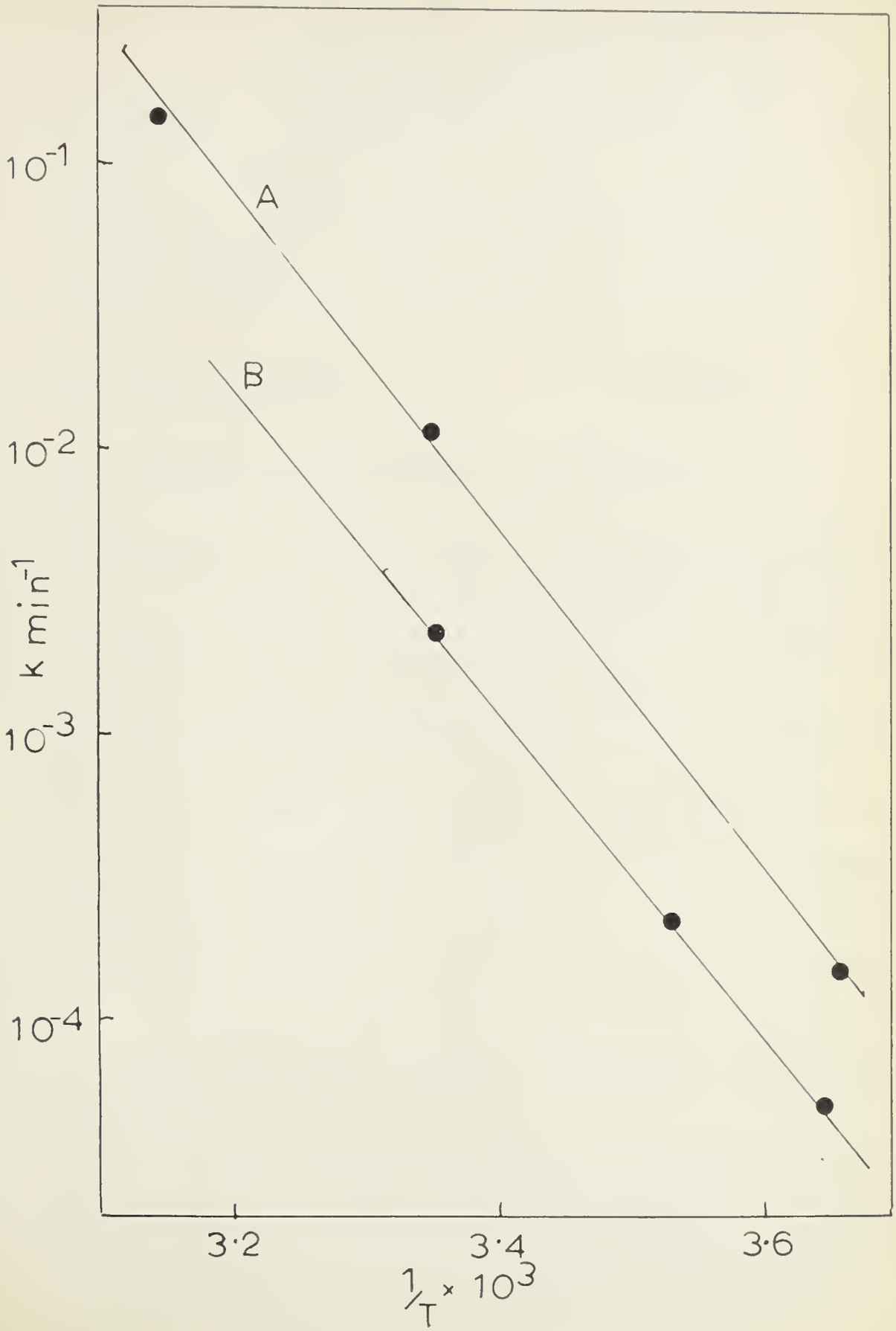

A
B
10^{-1}
10^{-2}
10^{-3}
10^{-4}
k min^{-1}
3·2
3·4
3·6
$1/T \times 10^3$

TABLE XLVI

ACTIVATION ENERGIES, FREQUENCY FACTORS AND ENTROPIES OF ACTIVATION FOR THE BASE HYDROLYSIS OF HALOPENTAMMINECHROMIUM (III) IONS

Reactant	$Cr(NH_3)_5Cl^{++}$	$Cr(NH_3)_5Br^{++}$	$Cr(NH_3)_5I^{++}$
Activation Energy pH 11.5 + k cal.	26.7	26.8[a]	26.8
Frequency factor pH 11.5 + $mole^{-1}$ min^{-1}	5×10^{17}	8×10^{18}[a]	2×10^{19}
Entropy of activation entropy units	9.2	11.9[a]	15.8

(a) values obtained from Dr. W.E. Harris.

The activation energies for the base hydrolysis reaction as for the aquation, appears to be independent of the nature of the bond being broken. The constancy of the activation energy as the leaving group is varied from chloride to bromide to iodide does not necessarily mean that the mechanism of the reaction is independent of the bond energy, since it was shown earlier that solvation of the anion tended to cancel out the effects of differences in bond strength.

The constancy of the activation energy cannot, therefore, be said to imply a bi-molecular displacement mechanism.

Again, as for the aquation reaction the observed differences in rate with chloride, bromide, and iodide seem to originate from the differences in the entropies of activation.

Discussion

The activation energies for the aquation and base hydrolysis reaction differ significantly, i.e. about 22 k cals for the aquation reaction and 26.5 k cals for the base hydrolysis reaction. The base hydrolysis reaction is about 10^3 times faster than the aquation reaction. This can be accounted for in terms of the larger frequency factor for the base hydrolysis reaction. The differencein frequency factors for the base hydrolysis and aquation reactions are in agreement with what would be expected if the aquation reaction proceeded by an SN_1 mechanism, and base hydrolysis by an SN_2 mechanism. It is difficult to correlate the difference in activation energy between the aquation and base hydrolysis reaction on the basis of an SN_1CB mechanism for the base hydrolysis; as has been proposed for the base hydrolysis of cobalt (III) complexes. Unfortunately, there are not available reliable data on the activation energies for the base hydrolysis of cobalt (III) complexes.

The observation that the base hydrolysis reaction does not occur below a pH of 10, is a strong indication that the reaction involves a bi-molecular attack by hydroxide ion, as it is above this pH that appreciable concentration of the hydroxide is present.

For the corresponding cobalt complexes the base hydrolysis reaction contributes to the rate even at a pH of 3. The rate of the base hydrolysis reaction of cobalt is approximately 10^7 times faster than the aquation reaction,

whilst the difference for the chromium complexes is only about 10^3. Chromium complexes aquate faster than the analogous cobalt complexes whilst the opposite is true for the base hydrolysis reaction.

On the basis of crystal field theory, it would be expected that chromium would react faster than cobalt by an SN_2 mechanism. Chromium with only 3 d electrons in the t_{2g} orbitals, compared to cobalt which has 6 d electrons would be expected to be more easily attacked by a nucleophilic ion, such as hydroxide.

Since cobalt complexes undergo base hydrolysis much faster than chromium complexes it would appear that an SN_2 mechanism is not operating in both cases.

Basolo and Pearson (24) interpret the strong reactivity of the cobalt complexes on the basis of the C.B. mechanism, as due to π bonding, resulting in repulsion between the π bonding electrons of the amido or hydroxy group, with a filled d_{xy} metal orbital.

If π bonding of this type is important for the chromium complexes with only 3 d electrons, the repulsion would not be as great, thus the conjugate base formed would not be as reactive, and the reaction consequently slower. It is possible to account for a slower rate for the base hydrolysis of chromium complexes, in comparision with cobalt, on the basis of an SN_1CB mechanism for both complexes. There is, however, no conclusive proof that the cobalt complexes base hydrolyse by an SN_1CB mechanism.

On the basis of the experimental data presented, it is believed that the base hydrolysis of halopentammine-chromium (III) complexes involve a bimolecular displacement SN_2 mechanism.

VII OBSERVATIONS ON THE DECOMPOSITION OF HYDROXOPENTAMMINECHROMIUM (III) COMPLEX

When following the aquation of the bromopentamminechromium (III) complex in the presence of various organic anions, it was observed that the total height of the polarographic wave, due to the reduction of both bromo and aquo complex, decreased with time. This was believed to be due to the fact that the aquo complex, formed as the product of the aquation of the bromo complex, was undergoing a subseauent reaction in the presence of anions.

In the literature, there is reported only two investigations on the decomposition of $Cr(NH_3)_5 H_2O^{+++}$ in aqueous solution. (88) (89) Bjerrum and Jorgensen (88) measured the rates of decomposition of the chromium (III) ammines, both in acid and basic solutions. In 0.4 M HNO_3 at 40°C the rate of decomposition of $Cr(NH_3)_5 H_2O^{+++}$ was found to be 1.41×10^{-3} min^{-1}, and in basic solution (0.1M NaOH) 6.0×10^{-4} min^{-1}. The rate of decomposition of $Cr(NH_3)_5 OH^{++}$ is in agreement with that obtained by Yoneda (89) i.e. 5.7×10^{-4} min^{-1} in 1.0M NaOH. Bjerrum followed the reaction by separating the lower ammine complexes on an alumina column, using different eluents. The concentration of the complex was then measured spectrophotometrically. Yoneda followed the reaction by filtering the precipitated metal hydroxides, and measuring the optical density of the resulting clear solution. Measurements on the solution done at several wavelengths revealed no shift in the absorption maxima. This indicated that the filtered solutions contained only the initial complex. Contrary to what would be expected

the hydroxopentammine complex decomposes more slowly than the aquopentammine. Since there appears to be a difference between the rate in acid and alkaline solution, it was decided to investigate the effect of pH on the aquation of $Cr(NH_3)_5H_2O^{+++}$ and $Cr(NH_3)_5OH^{++}$.

In acid solution, there appears to be little or no change in the height of the aquo wave with time, and only one wave is observed. This is believed to be due to the fact that the decomposition products of the $Cr(NH_3)_5\ H_2O^{+++}$, i.e. diaquotetrammine and triaquotriammine salts, are reduced at the same potential as the aquopentammine complex. Maki, Shimura and Tsuchida (90) found that this was the case for various substituted amminethiocyanatochromium (III) complexes. It was therefore not possible to follow the decomposition of $Cr(NH_3)_5\ H_2O^{+++}$ in acid solution by a polarographic technique. In basic solutions, pH greater than 7, it was possible to follow the decomposition of $Cr(NH_3)_5\ OH^{++}$, as the intermediate ammines were rapidly hydrolysed, and precipitated out of solutions as insoluble chromium hydroxide species. When the solution was acidified, these precipitated species were not taken back into solution, and as a consequence, the residual original complex in solution was determinable by a straight forward polarographic technique. In this way, it was possible to follow the decomposition of the hydroxy complex at any pH above 7.

The reaction followed an approximate first order path provided the buffer used was of such concentration, that

the pH of the solution did not change during the reaction. The rate of reaction at different values of pH in the pH range 7 to 13 at 25°C are reported in table (XLVII)

TABLE XLVII

EFFECT OF pH ON DECOMPOSITION OF $Cr(NH_3)_5 OH^{++}$ AT 25°C

pH	Buffer used and concentration	k min^{-1}
≃ 1.0	4M HNO_3; 4M $NaNO_3$	≃ 2×10^{-4} (a)
7.0	2-amino pyridine	9.96×10^{-4}
8.0	ammonia buffer (0.1M)	7.8×10^{-4}
9.0	ammonia buffer (0.1M)	$x.6 \times 10^{-4}$
10.0	ammonia buffer (0.1M)	1.15×10^{-4}
11.0	diethylamine (0.1M)	1.2×10^{-4}
12.0	.01M NaOH (0.2M $NaClO_4$)	7.0×10^{-5}
13.0	0.1M NaOH, 0.1M $NaClO_4$	2.65×10^{-5}
13.0	.1M NaOH	3.1×10^{-5} (b)
14.0	1M NaOH	3.0×10^{-5} (c)

(a) calculated from ref. (88) using activation energy of 22 k. cals.

(b) from ref. (89)

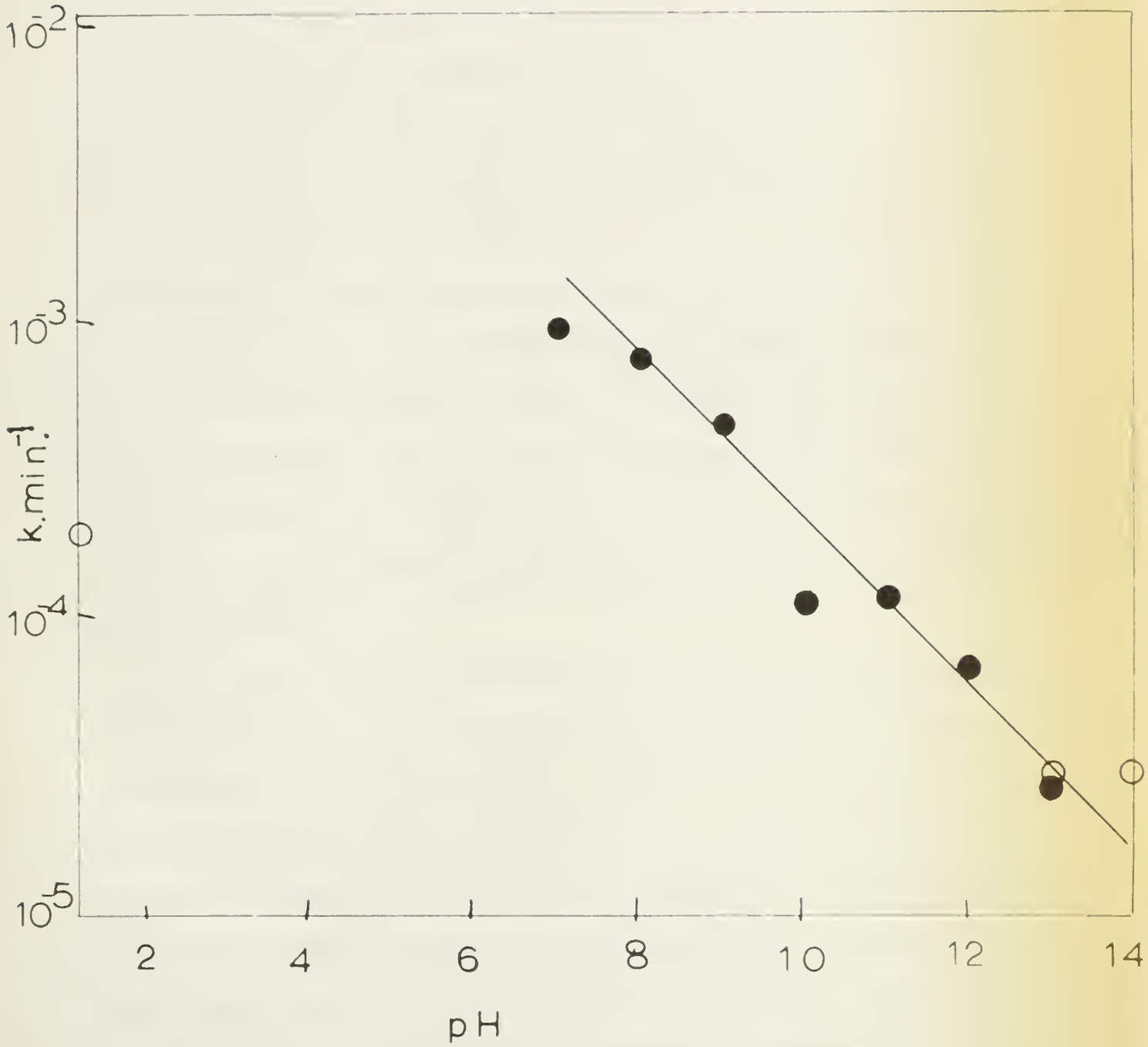
(c) from ref. (88)

Figure 33 shows a plot of the rate constant against pH. The rate appears to change almost linearly with pH over the pH range 7 to 13. It was not possible to obtain values for the rate constant in acid solution. Bjerrum reports a

Figure 33

Plot of the pseudo first order rate constant for the decomposition of $Cr(NH_3)_5 OH^{++}$ against pH at 25°C.

The data represented by the open circles were obtained from references (88) and (89).


10^{-2}
10^{-3}
10^{-4}
10^{-5}
k.min^{-1}.
2
4
6
8
10
12
14
pH

value of 1.41×10^{-3} $mins^{-1}$ for the rate in .4M HNO_3 solution at 40°C. Since the activation energy of the reaction is not known, it is not possible to calculate what the rate would be at 25°C. It can, however, be safely argued that the rate would be decreased by a factor of about 10 in going from 40°C to 25°C. This is based on the activation energy being about 22 k cals. From fig. 33 it would, therefore, appear that the rate goes through a maximum as the rate at pH 7 is approximately 10 times faster than that expected at a pH of 1. This observation is rather surprising and cannot be explained in terms of straight forward aquation of the aquo and hydroxo complexes. If the only reactions taking place were the aquation of the aquo and hydroxo complex, with the aquo complex being the more unstable, then, a pH dependence would be expected only when both aquo and hydroxo complex were present. This pH dependence should also only be observed in the pH range 7.5 to 8.5, since the acid ionization constant for $Cr(NH_3)_5H_2O^{+++}$ is 6.3×10^{-6}.

The rate of reaction is not first order in hydrogen ion concentration as is shown in fig. 33. This would suggest that there are at least two reactions taking place simultaneously, of which one is pH dependent. The possibility of reaction between two moles of the hydroxo complex or between aquo and hydroxo complex to give binuclear complexes can be eliminated since the reaction follows a first order path and not second. At this stage it is not possible to explain the observed pH effect on the reaction. However, this investigation has shown that the rate of decomposition of the aquo

complex was slow compared with the rates of aquation which have been observed. As a consequence, it can be asserted with confidence that the reaction studied is in fact accurately represented by equation XCV.

$$Cr(NH_3)_5\,Br^{++} + H_2O \longrightarrow Cr(NH_3)_5\,H_2O^{+++} + Br^- \qquad \text{(XCV)}$$

Such side reactions as the decompositon of the aquo complex are much slower, and do not have to be taken into account in the interpretation. In order to understand the processes which lead to the complete decomposition of the complex it would be desirable to study the reaction in the acid region. Such a study would necessitate the separation and identification of all the products of the reaction. Since we were interested in the effect of citrate on the decomposition of the hydroxo complex, this was investigated both at pH 9.2 and 8.5. This pH range was chosen so as to reproduce the conditions under which the aquation of the halopentammine complexes were investigated.

A plot of the pseudo first order rate constant against concentration of added citrate is shown in fig. 34 for both pH 8.5 and 9.2. The date for fig. 34 are reported in table XLVIII.

The effect of citrate on the reaction rate is very similar to its effect on the rate of aquation of the halo complexes (fig. 18 and 19).

As for the aquation of the halo complexes it is believed that the curves in fig. 34, represent the formation of

TABLE XLVIII

EFFECT OF CITRATE CONCENTRATION ON DECOMPOSITION OF $Cr(NH_3)_5OH^{++}$ at 25°C in .01M NH_4ClO_4 / NH_4OH BUFFER.

pH	Sodium Citrate Concentration	k min^{-1}
8.5	----	7.5×10^{-4}
	.001	1.04×10^{-3}
	.005	2.2×10^{-3}
	.01	2.8×10^{-3}
	.04	5.8×10^{-3}
	.07	6.7×10^{-3}
9.2	----	5.0×10^{-4}
	.001	5.4×10^{-4}
	.005	6.7×10^{-4}
	.01	8.6×10^{-4}
	.10	2.4×10^{-3}

ion pair between the hydroxo complex and citrate at low concentrations of citrate. The decrease in the slope at higher citrate concentrations represents the effect of ionic strength on the ion pair constant.

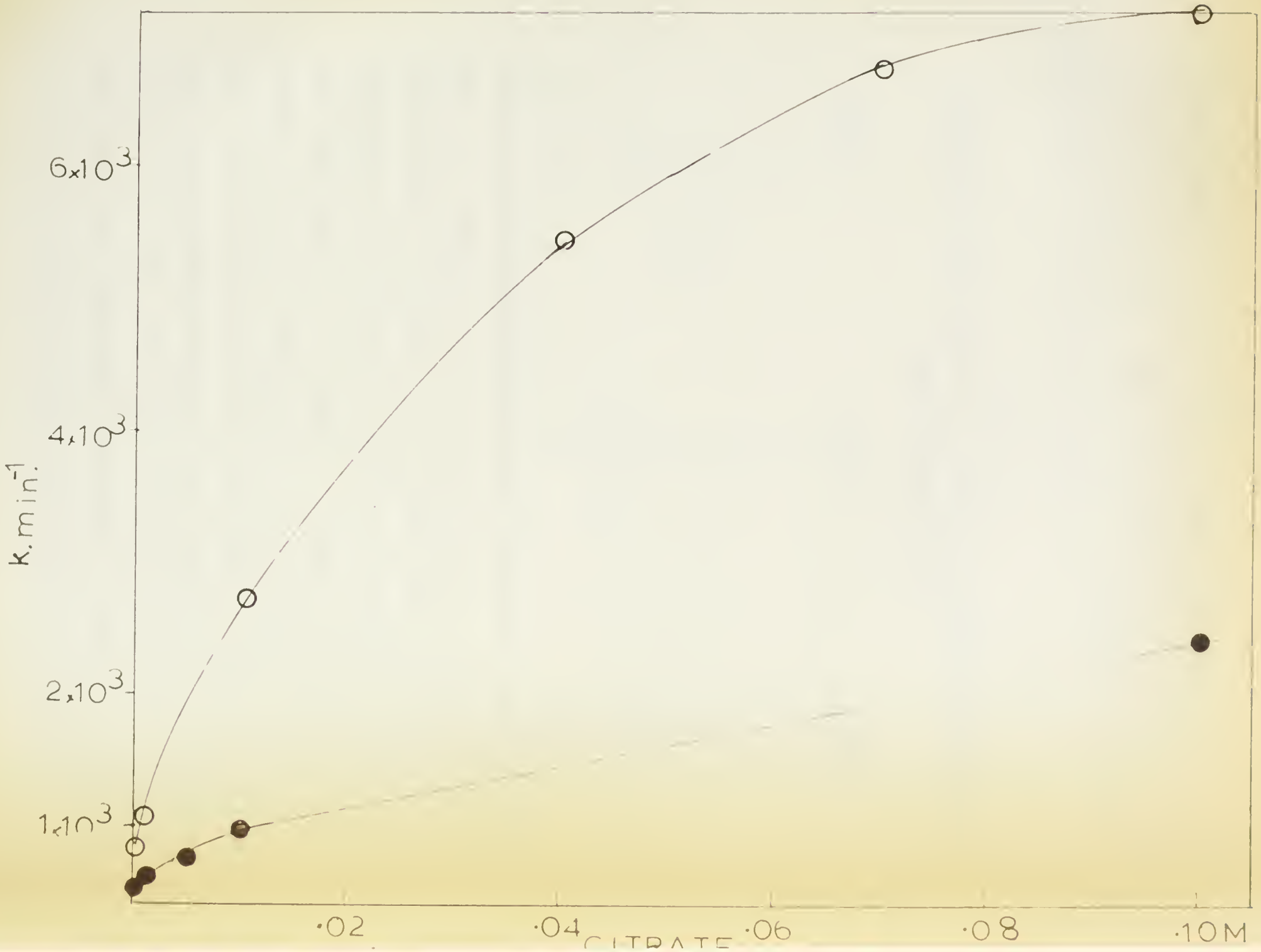
It was observed that the precipitation found in the case of the uncatalysed decomposition reaction did not occur in the presence of citrate. The colour of the solution changed from the purple colour of the hydroxo complex to a very much

Figure 34

Plot of the pseudo first order rate constant for the decomposition of $Cr(NH_3)_5 OH^{++}$ at pH 8.5 and o.2 against citrate concentration at 25°C.

A pH 8.5

B pH 9.2


6x10^3
4x10^3
2x10^3
1x10^3
k.min^-1
·02
·04
·06
·08
·10M
CITRATE

lighter purple bluish colour. Table XLIX shows the change in λmax (wavelength of maximum absorption) during the reaction of citrate with $Cr(NH_3)_5 OH^{++}$. As reaction proceeds λmax shifts to shorter wavelengths.

TABLE XLIX

CHANGE IN λ MAX DURING THE REACTION BETWEEN $Cr(NH_3)_5 OH^{++}$ AND CITRATE AT 30°C

Time	max peak 1	max peak 2
0	491	367
30 min.	497	371
2 hr. 20 min.	503	373
7 hr. 30 min.	505	375
23 hr.	2 peaks (composite)	380
48 hr.	568	407

This would suggest that a citratochromium complex is formed. The spectrum of a solution of $Cr(NH_3)_5OH^{++}$ and sodium citrate which had been allowed to stand for 48 hours at 30°C was identical with that for the reaction between aquochromium with citrate. For the decomposition of $Cr(NH_3)_5 OH^{++}$ only one wave, due to the reduction of the hydroxo complex is observed. The citratochromium complex is not reduced at the dropping mercury electrode. It would, therefore, seem that citrate does enter into the complex and that its entry is facilitated by ion pair formation between the complex and citrate.

It is not understood why the effect of citrate on the reaction rate seems to be dependent on the pH of the solution fig. 34. At pH 9.2 the rate is increased only a factor of six in 0.1M sodium citrate, whilst at pH 8.5 the rate is increased almost twenty times. That the reaction does involve a direct attack by the citrate on the complex, is confirmed by the fact that the reaction is not first order in citrate concentration.

From the effect of sodium citrate on the decomposition of $Cr(NH_3)_5 OH^{++}$, it can be concluded that citrate catalyses the reaction. The product of the reaction appears to be a citratochromium (III) complex which is not reduced at the dropping mercury electrode. The rate of disappearance of the aquo complex is slower than the rate of aquation of $Cr(NH_3)_5Br^{++}$. It can, therefore, be concluded that the catalysing effect of citrate on the rate of reaction of the bromo complex is not due to penetration of the complex by citrate, but by ion pair formation which facilitates removal of the halide ligand to give the aquo complex. Another possibility for the mechanism of citrate catalysis of the aquation of $Cr(NH_3)_5 Br^{++}$ is, that initially a citrate molecule enters into the complex to displace the halide ligand. This is then followed by a rapid step in which water displaces the citrate to give the aquo complex. On the basis of the results reported here, this mechanism appears unlikely, since the rate of entry of citrate into the complex is slow. Also, once the citrate complex is formed it is very stable.

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